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if things only fragmentary and imperfect, and it has not been possible to suggest a reason why compounds containing the grouping $\text{O}\cdot\text{NH}\cdot$ or $\text{CO}\cdot\text{O}\cdot$ should form series so different in character from other series. The Quantum Theory has not yet been extended to include the investigation of complex molecules, but there is no doubt that a knowledge of the vibration frequency (ν), and the specific heat over a wide range of temperature, is essential for a complete mathematical treatment. The determination of the melting points of a large group of similar compounds is at all events a step in this direction.

My thanks are due to Dr. P. A. Levene for a specimen of tridecoic acid, and to the Chemical Society for a grant, which has partly defrayed the cost of the investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.

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CXII.—*The Effect of Sea-salt on the Pressure of Carbon Dioxide and Alkalinity of Natural Waters.*

By EDMUND BRYDGES RUDHALL PRIDEAUX.

THE total "uncompensated base" or alkali present as carbonate and hydrogen carbonate in sea-water has been determined by Schloesing and Dittmar and by many later investigators. The method used is nearly always titration with standard acid and an indicator of the methyl-orange class, and is subject to the errors of such titrations. The results, expressed in milli-equivalents per litre, are 2.48 (Schloesing) and 2.41 (Dittmar). Moore, Herdman, and the author found values ranging from 2.36 to 2.50 (extreme values), average 2.44, in the water of the Irish sea from November, 1912, to July, 1913 (Herdman, "Report on the Lancashire Sea-Fisheries Scientific Investigations for 1914," *Trans. Biol. Soc. Liverpool*, 1915, 29).

Fox (*Trans. Faraday Soc.*, 1909, 5, 68), by boiling with excess of standard hydrochloric acid and titrating with standard sodium hydroxide and phenolphthalein, found the equivalent of 40 milli-grams of hydroxylion on the average, or 2.35 milli-equivalents. The author, in June, 1913, using the same method, found 2.30.

The total carbonic acid may be obtained by boiling with an excess of sulphuric acid in a current of air and absorbing the carbon dioxide in standard barium hydroxide solution. In nearly all cases, however, the alkali of the carbonate and hydrogen carbonate, and hence the total carbon dioxide, has been obtained from the titrations with phenolphthalein and methyl-orange, the difference between these (in equivalents) being numerically equal to the number of molecules of carbonic acid present. The amount of water taken in the work referred to above is 100 c.c., to which five drops of 0.1 per cent. phenolphthalein are added, and the acid ($N/100$ - or $N/50$ -hydrochloric acid) is run in until the colour completely disappears. Then five drops of 0.1 per cent. dimethyl-aminoazobenzene or methyl-orange are added, and the titration is continued to a decided reddish-orange. With regard to the phenolphthalein titration, it may be remarked that in fresh water $N/10$ - down to $N/1000$ -hydrogen carbonate solutions are still slightly alkaline to phenolphthalein ($p_H=8.4$ to 8.2), and the titration should therefore be continued until a weak colour remains. In the case of sea-water, however, the p_H by extrapolation of the values given later and by direct measurement (see below) is 7.6. This, owing to the presence of salt, will appear to have a p_H of about 7.8. Consequently, the titration should be continued until the solution is quite colourless. The methyl-orange titrations in dilute solutions, and especially in such as contain salt, are likely to be high. This was verified in the standard carbonate solutions and neutral sea-water, and it was found that from 1 to 2 c.c. of $N/100$ -hydrochloric acid should be subtracted from the titrations of 100 c.c. Thus the total alkali is probably 2.24 to 2.34 milliequivalents per litre. Since the number of c.c. of $N/100$ -acid required in the phenolphthalein titration is from 1 to 3 for 100 c.c. of water, that is, 0.1 to 0.3 milliequivalents per litre, the value of R =equivalents of alkali÷molecules of carbonic acid is from $2.3/2.2=1.04$ to $2.3/2.0=1.15$. It may be noted that Schlösing found carbonic acid equivalent to 98.3 milligrams of carbon dioxide and alkali equivalent to 99.3 milligrams of SO_3 , from which $R=1.12$.

The alkalinities corresponding with all stages of neutralisation of carbonic acid at different concentrations have already been expressed as general equations (*Proc. Roy. Soc.*, 1915, [A], 91, 535), and those which refer to the dilute solutions contain only the dissociation constants of carbonic acid and the water constant, together with the experimental quantities C =total concentration of carbonic acid and R the ratio of alkali to acid. From the curve (*loc. cit.*) connecting p_H and R , which agrees well with the

experimental alkalinities of hard water, etc., the following values have been taken in the row of calculated values:

<i>C.</i>	<i>R</i> =	1.06	1.08	1.10	1.12
0.001	<i>p_H</i> =	9.0	9.15	9.25	9.35 (calculated)
0.002	<i>p_H</i> =	8.7	8.9	8.95	8.9 (observed)

Obviously, the alkalinities are much greater than those found in the case of the same carbonate solutions present in sea-water. It seemed desirable to check experimentally this part of the curve in the case of fresh water.

Standard carbonate solutions were prepared by methods independent of indicators and titrations. Some *M*/10-sodium carbonate was made in the usual way. The factor, from the weight of sodium carbonate, was 1.015, by conversion into sodium sulphate 1.016, and by titration, using methyl-orange, 1.018. Some *N*/10-hydrochloric acid made by dilution from a known standard and again analysed by conversion into silver chloride had a factor of 1.000. Mixtures (1), (2), (3), (4) were made from these by adding to 50 c.c. of the *M*/10-sodium carbonate 47.75 c.c., etc., of the hydrochloric acid in order to produce solutions of ratios 1.06, etc., as above. These were kept in tightly corked flasks. So many c.c. were taken as contained the equivalent of 2.2 c.c. of *N*/10-alkali [for example, of mixture (1) 4 c.c.] and made up to 100 c.c. with distilled water free from carbon dioxide. These solutions were all 0.0022*N* with respect to alkali and 0.0021 to 0.00196*M* with respect to carbonic acid. Measured amounts of phenolphthalein were added, and the samples matched against the Sørensen borate-hydrochloric acid standards. The results are given in the third row above. The curve for *C*=0.002 should fall slightly above that calculated for *C*=0.001; actually it is slightly low.

The connexion was then determined between *p_H* and *R* of sea-water, in which the value of *R* was accurately known. The same standard carbonate solutions were diluted with neutral sea-water instead of with distilled water.

Many experiments carried out with the view of depriving sea-water or sea-salt of its "uncompensated base" and leaving it in neutral condition were not sufficiently successful to warrant the use of such water in investigating the effect of adding such small quantities of carbonates and hydrogen carbonates. An artificial *rimé* was therefore made from the crystallised salts, which possessed the average composition given in Clarke's "Data of Geochemistry," but omitting the potassium salts and others present in such small amounts that they were likely to have a negligible effect on the

alkalinities. This water was tested for neutrality by means of rosolic acid, which gave a yellow colour quite indistinguishable from that of a standard neutral solution having $p_H=7.07$. The addition of 0.2 c.c. of $N/100$ -hydrochloric acid and $N/100$ -sodium hydroxide to this water (10 c.c.) produced a perceptible change of colour, showing that the brine contained no appreciable amount of hydrolysed salts or hydrion regulator.

The solutions were then made up from the standard carbonates and this salt water as before. To 10 c.c. were added eight drops of 0.1 per cent. phenolphthalein or six drops of 0.04 per cent. α -naphtholphthalein. The salt error of the former is about 0.2 in p_H , and that of the latter is the same to a sufficiently close approximation (Sørensen). The hydrion standards used for comparison were (1) the borate-hydrochloric acid mixtures of Sørensen, (2) the partly neutralised mixture of phosphoric, acetic, and boric acids, which were previously found by the author (*Proc. Roy. Soc.*, 1916, [A], 92, 463) to replace suitably the borate standards from $p_H=8.3$ to 8.0. The results are as follows:

$R=$	1.06	1.08	1.10	1.12
p_H found.....	8.1	8.3	8.35	8.3
p_H corrected for salt...	7.9	8.1	8.15	8.1

As in the case of the water without salt, there is practically no change in the alkalinities between $R=1.08$ and $R=1.12$.

This was the case also both in the fresh and salt solutions having $R=1.16$.

On the average, then, p_H is 8.9 in fresh water containing hydrogen carbonate and carbonate of these ratios and carbonic acid at a total concentration of about 0.002 mol., whilst it is 8.1 in salt water, which is identical with respect to alkali and carbonic acid. This effect might, of course, be referred to the less complete primary ionisation of the hydrogen carbonate and carbonate in the presence of so much salt, leading to a diminished hydrolysis. The experimental fact, however, in itself seems to involve biochemical and geochemical consequences, which will be considered after some results on the equilibrium with atmospheric carbon dioxide.

The question whether sea-water is or is not saturated with atmospheric carbon dioxide has been much discussed. Fox (*loc. cit.*) has made a most useful series of observations of the actual pressures of carbon dioxide in equilibrium with waters of varying salinity. The values of hydrion were not then fully available as at present. Obviously there is a relation between hydrion content and pressure of carbon dioxide, and, indeed, from the data

at present available it should be possible to calculate the latter from the values for hydron, R , etc. There are still, however, difficulties in the way of doing this, except by empirical equations. Some simple experiments carried out in the spring of 1919 at Port Erin throw some light on this question. Pure air, taken from outside the laboratory, was bubbled through sea-water for periods varying from a few hours to twenty-four and twenty-seven. The value of p_H found in this water was always 8.1.

Numerous blank experiments were being made during this period on the sea-water freshly drawn, and the p_H values varied between 8.2 and 8.3. This alkalinity was preserved when the water was allowed to remain motionless for a day or more in the laboratory. Thus, the sea-water when exposed to a current of air gained carbon dioxide in every case, and this although the alkalinity was distinctly low for the time of year, since the surface water had been mixed with the lower layers and brought into better contact with the air by recent storms. The usual range in sea-water is from 7.95 to 8.35, but values below $p_H=8.1$ are exceptional in the case of surface waters, although they have been found in the Skager Rack and off the coast of Norway.

According to the above experiments, all waters of higher alkalinity than $p_H=8.1$, that is, nearly all surface waters, will gain carbon dioxide from the air. The experiment was repeated on the artificial sea-water, which was made up with carbonates so that p_H was 8.2. By saturation with a current of air, this was reduced to 7.9 or 8.1 as measured by different standard solutions and indicators. From the measurements of the neutral sea-water containing known amounts of alkali and carbonic acid, it is seen that $p_H=8.1$ in salt water corresponds with a ratio of about 1.08, and therefore any sea-water containing less than $2.2/1.08=2.04$ millimols. of carbonic acid to 2.2 milli-equivalents of alkali should gain carbon dioxide from the air.

This result may be compared with a deduction from Fox's measurements of the absorption of carbon dioxide in salt waters of varying salinity and alkalinity. The "physically dissolved" carbon dioxide is expressed as c.c. of the gas " a " dissolved at different temperatures for each 0.01 per cent. of carbon dioxide in the air. Thus, for his highest salinity=20 per cent. of chlorine, which is nearly equal to that of the artificial salt water of the present work, $pa=3 \times 0.0875=0.2625$ c.c. per litre of water at $t=16^\circ$ and $p_{CO_2}=0.0003$ atmosphere.

The carbon dioxide combined with alkali " b " is given for each milligram of alkali expressed as hydroxyl and for each pressure and temperature of carbon dioxide. At $t=16^\circ$ and $p_{CO_2}=0.0003$

atmosphere, b is 1.18. Taking Fox's value of the total alkali = 40 milligrams of hydroxyl, or 2.35 milli-equivalents, the total carbon dioxide = $0.26 + (1.18 \times 40)$ c.c.:

$$R = \frac{\text{equivalents alkali}}{\text{mols. of carbonic acid}} = \frac{40 \times 22.4}{17 \times 47.46} = 1.11.$$

If the sea-water has a total alkalinity of 2.2 milli-equivalents, or 37.4 milligrams of hydroxyl, R becomes 1.05. The value of R in equilibrium with air is not greatly affected by changes of temperature; thus 1.11 at 16° becomes 1.09 at 12° and 1.115 at 18°.

Thus the direct experimental result is confirmed that, in a water of total alkalinity equal to 2.2 milli-equivalents, the lowest ratio and the highest acidity that is normally encountered in sea-water is only just in equilibrium with atmospheric carbon dioxide, and that in all other cases the water will gain carbon dioxide.

The surface waters of the sea gain carbon dioxide, not only from the air, but also by mixture with the subjacent layers in which low values of p_H are almost invariably found, and likewise by the decay of plants. It is apparently only the photosynthetic action of seaweeds, plankton, etc., which maintains alkalinities of more than 8.1 in the surface waters. There is no known inorganic chemical agency which is capable of doing this. At the same time, since the pressure of carbon dioxide in the sea becomes greater than that in the atmosphere at alkalinities below $p_H = 8.1$, the alkalinity of surface waters cannot fall much below this point.

The alkalinity of bicarbonated fresh waters is also kept at about $p_H = 8$, but by a different chemical equilibrium. In these cases, the ratio R , as defined above, is 1.00, and this, from the curve already quoted, corresponds with $p_H = 8.2$. Solutions which have the higher ratios found in sea-water, namely, 1.06 to 1.16, and contain quite an appreciable amount of carbonate, could not long exist in fresh water: they give a strong pink colour with phenolphthalein, as already determined, and would rapidly gain carbon dioxide from the air, and probably also in many cases deposit calcium carbonate or basic magnesium carbonates. The converse effect is best seen by noting the probable course of events when a fresh water of temporary hardness 11, consisting of hydrogen carbonates having the same total alkali concentration as the sea, becomes mixed with it. The static acidity would be greatly raised: thus, if the salt could be added to the original hydrogen carbonate, p_H would fall to 7.6. This was found by an experiment in which the calculated quantities of the standard carbonate and hydro-

chloric acid were added to the neutral sea-water and the colour given with α -naphtholphthalein was matched against a "mixed acid" alkali standard. By the mixture of equal volumes of the fresh water and sea-water, the alkalinity would assume an intermediate value, and one lower than that in normal surface waters, whilst the pressure of carbon dioxide would be correspondingly high, and carbon dioxide must be given up to the air or to other large quantities of water until R rises again to 1.05. It is quite possible that the higher acidities and pressures of carbon dioxide which have been observed everywhere below the surface are due mainly to this cause—the continued addition of bicarbonate waters—without any adequate opportunity of yielding up the excess of carbon dioxide from such immense masses of water. It may also be noted that were it not for the effect of salt in raising to such a high degree the acidity and pressure of carbon dioxide which correspond with a given proportion of alkali and carbon dioxide, the sea would contain much more carbon dioxide than it actually does. Thus, if it consisted of a dilute hydrogen carbonate solution, such as a hard water in equilibrium with the air, it would contain about 5.5 per cent. more carbon dioxide combined with the same quantity of alkali. Since the total carbon dioxide is about 50 c.c. per litre, every cubic metre of sea-water would contain 2.25 litres of carbon dioxide more than at present. The relative availability for plant life of the carbon dioxide in fresh and salt waters is a different question. As shown by Moore and his collaborators (*loc. cit.*), the flora of the sea can use the carbon dioxide of the hydrogen carbonate to a certain limit which approximately corresponds with the production of carbonate. Now, owing to the effect of the salt, sea-water in equilibrium with the air already has a ratio of 1.04 to 1.06; there is some carbonate present. The alkali present in fresh water in equilibrium with the air, and of almost the same alkalinity, is practically all as hydrogen carbonate. Therefore, in the fresh water of the same total alkalinity, for example, 2.2 milli-equivalents per litre, there is more carbon dioxide available before the carbonate point is reached. On the other hand, far more carbon dioxide can be abstracted from sea-water without an excessive rise of alkalinity.

A sea-water of original ratio 1.06 $\left(= \frac{1}{0.945} \right)$ can, by abstraction

of carbon dioxide, have R changed to 1.16 $\left(= \frac{1}{0.862} \right)$, losing 8.7

per cent. of the original carbon dioxide, and still only have an alkalinity corresponding with $p_H = 8.35$. A fresh water of original ratio 1.00 can have this changed to $R = 1.06$ by losing 5.5 per

cent. of the original carbon dioxide, but this changes the alkalinity to the high value corresponding with $p_H=8.7$.

The author desires to make grateful acknowledgment of the assistance given by the Percy Sladen Memorial Trust towards this research.

MARINE BIOLOGICAL STATION,
PORT ERIN, ISLE OF MAN.

UNIVERSITY COLLEGE,
NOTTINGHAM.

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CXIII.—*The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Water-Acetone Mixtures.*

By GEORGE JOSEPH BURROWS.

IN a previous paper (T., 1914, 105, 1260) the author recorded some experiments on the inversion of sucrose by acids in water-ethyl alcohol mixtures. It was there found that the rate of inversion at first decreased slightly as water was replaced by alcohol up to about 50 per cent. of alcohol, and then increased. It was concluded from the results that the catalytic activity of the acid was really greater in alcohol than in water, and that the addition of water had a depressing effect on the rate of hydrolysis. At the same time, the author was unable to explain the decrease in the rate of inversion which results from the replacement of water by alcohol up to 50 per cent. mixtures without assuming that the mixed solvents had some specific effect on the rate of reaction, and it was there suggested that this was due to a change in the fluidity of such mixtures, causing a variation in the rate of catalysis similar to that observed in conductivity.

In obtaining the results in that work, the reaction was treated as a unimolecular one, the concentration of the water being neglected. This assumption was made in view of the fact that even in a solution containing 75 per cent. of alcohol by volume the ratio of the number of molecules of water to molecules of sugar present at the commencement of the reaction was 45, so that the decrease in concentration of the water during the reaction was only $1/45$ of its original value. In a 50 per cent. alcohol mixture the ratio was 91. Under these conditions, it was considered that the concentration of the water could be omitted from the equation and the reaction considered as unimolecular.

If, however, the concentration of the water is considered, the value of k_1 , calculated from the bimolecular equation

$$k_1 = \frac{1}{t(w-b)} \log \frac{b(w-x)}{w(b-x)}$$

(where b and w are the number of gram-molecules of sugar and water respectively in the solution at the beginning of the reaction), is, of course, much smaller than the corresponding value of k obtained from

$$k = \frac{1}{t} \log \frac{b}{b-x}$$

In this case, the total concentration of water is considered to represent its mass as one of the active substances, irrespective of the fact that it is present in large excess and only a small fraction of the total concentration is used up during the reaction.

The difference between the values of k and k_1 is shown in the following table:

Sucrose (10 per cent.) and N/2-Hydrochloric Acid at 25.0°.

Alcohol (volume per cent.).	k .	k_1 .
0.0	0.00219	0.0000427
16.7	0.00213	0.0000491
25.0	0.00204	0.0000519
40.0	0.00192	0.0000607
50.0	0.00176	0.0000667
60.0	0.00185	0.0000877
75.0	0.00208	0.0001603

It will be seen that whereas the values of k pass through a minimum for a certain mixture, the values of k_1 steadily increase.

It appeared of interest to see if similar results would be obtained in the case of ester hydrolysis, and with this end in view experiments have since been performed on the rate of hydrolysis of methyl acetate by hydrochloric acid. Owing to its effect on the equilibrium, alcohol could not be used as one of the solvents in this research, so that the experiments were performed in mixtures of acetone and water. Acetone undergoes change under the influence of the acid used in the hydrolysis, but it has been assumed that this has no effect on the rate of hydrolysis of the methyl acetate.

The acetone used in these experiments was dried over and distilled from calcium chloride. The methyl acetate was freed from acetic acid by means of sodium carbonate and was distilled from calcium chloride; it was neutral to litmus. The volume of the

solution was adjusted at the temperature of the experiment, which was 25° in every case. The acetone percentages given are by volume; thus 70 per cent. acetone was prepared by mixing seven volumes of acetone with three of water. In preparing a 5 per cent. solution of methyl acetate for hydrolysis by $N/2$ -hydrochloric acid in 70 per cent. acetone, the following method was adopted: 10 c.c. of methyl acetate were diluted to 100 c.c. at 25° with 70 per cent. acetone (A), 20 c.c. of 5*N*-hydrochloric acid were mixed with 46.7 c.c. of anhydrous acetone, and the mixture was diluted to 100 c.c. at 25° with 70 per cent. acetone (B). Equal volumes of (A) and (B) were then mixed in a dry flask and placed in a thermostat at 25°. The weights of water and acetone used in preparing the solutions were also determined, so that all concentrations can be expressed in terms of gram-molecular weights. The reaction was followed in the usual way by titrating 5 c.c. of the solution under investigation with baryta solution after different intervals of time, the increase in titre indicating the concentration of the acetic acid produced. At first the reaction was treated as unimolecular, and the values of k were calculated from the equation

$$k = \frac{1}{t \sqrt{4bn+1}} \log \frac{4bn+2nx(\sqrt{4bn+1}-1)}{4bn-2nx(\sqrt{4bn+1}+1)} \quad (1)$$

obtained by integrating $\frac{dx}{dt} = k(b-x) - k_2x^2$.

In this equation $n = \frac{b-\xi}{\xi^2}$, where ξ represents the amount of ester which actually undergoes hydrolysis up to the equilibrium, b is the initial concentration of ester, and x the amount hydrolysed in time t . It was found that the above equation gave values of k which were quite constant for any particular solution. However, in the case of a series of experiments in different water-acetone mixtures, it was found that as the water was replaced by acetone the value of k at first decreased and then increased.

Owing to the relatively small concentration of water in solutions containing a high percentage of acetone, it was then decided to calculate all results also from the equation for a bimolecular reaction. The equation used was that given by Griffith and Lewis (T., 1916, 109, 69),

$$k_1 = \frac{1}{tA} \log \frac{A+y+2(K-1)x}{A-y-2(K-1)x} \cdot \frac{A-y}{A+y} \quad (2)$$

obtained by integrating $\frac{dx}{dt} = k_1(b-x)(w-x) - k_2x^2$,

where

k_1 = rate of hydrolysis,

k_2 = rate of esterification,

b = initial number of gram-molecules of methyl acetate in 1000 c.c. of solution,

w = initial number of gram-molecules of water,

x = number of molecules of ester decomposed in time t .

In equation (2),

$$y = (w + b)$$

$$A = \sqrt{(w + b)^2 + 4(K - 1)wb}$$

and
$$K = \frac{k_2}{k_1} = \frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{acetic acid}} \times C_{\text{alcohol}}} \text{ at equilibrium.}$$

The values of both k and k_1 obtained in any solution were found to be constant. This is seen in tables I and II, which contain the results for the hydrolysis of 5 per cent. methyl acetate by $N/2$ -hydrochloric acid in 80 and 90 per cent. acetone (by volume) respectively.

TABLE I.

80 Per cent. Acetone.

$$b = 0.6267; w = 10.20; K = 5.14.$$

t .	x .	$k_1 \times 10^5$.	$k \times 10^4$.
0	—	—	—
48.5	0.0506	7.41	7.51
78.5	0.0819	7.44	7.79
111	0.1095	7.43	7.56
138	0.1314	7.34	7.44
168	0.1575	7.44	7.55
228	0.1992	7.32	7.40
258	0.2200	7.36	7.43
318	0.2592	7.47	7.52
401	0.2983	7.31	7.35
α	0.4963	—	—
Mean ...		7.40	Mean 7.51

TABLE II.

90 Per cent. Acetone.

$$b = 0.6267; w = 4.752; K = 8.97.$$

t .	x .	$k_1 \times 10^5$.	$k \times 10^4$.
0	—	—	—
50	0.0636	19.77	9.35
85	0.0991	18.95	8.91
10	0.1262	19.35	9.08
140	0.1523	19.12	8.94
206	0.2018	18.91	8.80
263	0.2435	19.80	9.18
324	0.2695	19.34	8.94
400	0.2957	19.16	8.82
484	0.3102	19.63	9.00
α	0.3608	—	—
Mean ...		19.56	Mean 9.00

In table III is given a summary of results obtained for the hydrolysis of 5 per cent. methyl acetate by *N*/2-hydrochloric acid in different water-acetone mixtures. The value of *b* is 0.6267 in each case. The value of *K* was determined by ascertaining at the completion of the reaction the amount of acetic acid produced and then calculating the equilibrium constant. It was found that the numbers so obtained varied with the different solutions. This method of determining the conditions at equilibrium by analysing the solution actually used for the rate of hydrolysis is undoubtedly open to error, as a small amount of the volatile substances must escape each time the flask is opened to determine the concentration of acetic acid at each particular time. The amount lost in this way during a complete experiment would probably be sufficient to introduce an error into the value of *C* (acetic acid), and this might lead to quite a large error in the value of *K*. The variations in *K* are possibly due to a small error in the values of the concentrations of acetic acid found for the various solutions. At the same time, it has been found that a comparatively large difference in *K* produces only a small difference in the value of *k*₁. Thus the mean value of *k*₁ for a solution containing 90 per cent. of acetone is found to be 19.56 when *K* = 8.97 and 18.7 when *K* is taken as 5, the approximate value found in the other solutions.

In the latter case, however, the numbers obtained for *k*₁ decrease regularly, whereas if the experimental values of *K* are taken there is no such decrease. For this reason, it has been decided to employ the values of *K* actually found, although it is realised that the variation in its value for the different solutions may be due, in part at least, to the method of determination.

In the following table, the values under *k* are calculated from equation (1), those under *k*₁ from equation (2).

TABLE III.

Methyl Acetate (5 per cent.) and N/2-Hydrochloric Acid.

Acetone (volume per cent.).	Gram-molecules of acetone per litre.	<i>w</i> .	<i>K</i> .	<i>k</i> ₁ × 10 ⁴ .	<i>k</i> × 10 ⁴ .
0	0	52.32	5.40	2.76	13.58
20	2.665	42.46	5.10	3.03	12.28
40	5.39	32.08	4.38	3.38	10.33
60	8.10	21.23	4.47	3.86	7.91
70	9.42	15.72	4.51	4.56	7.05
80	10.66	10.20	5.14	7.40	7.51
90	11.84	4.752	8.97	19.56	9.00

It will be seen that the value of *k*₁ increases regularly as water is replaced by acetone as solvent. The values in the sixth column

under k , however, at first decrease as water is replaced by acetone and then increase.

A similar result was obtained for the hydrolysis of 2.5 per cent. methyl acetate by $N/10$ -hydrochloric acid. Owing to the small amount of methyl acetate actually present at equilibrium, the value taken for K for each of the solutions in this series was the value found in the corresponding solution with 5 per cent. methyl acetate and $N/2$ -hydrochloric acid.

TABLE IV.

Methyl Acetate (2.5 per cent.) and $N/10$ -Hydrochloric Acid.

In all cases, $b = 0.3133$ gram-molecules per litre.

Acetone. Per cent.	Gram-molecules of acetone.	w .	$k_1 \times 10^4$.	$k \times 10^4$.
0	0	54.00	4.78	2.60
20	2.73	43.97	5.40	2.39
40	5.53	33.44	5.76	1.90
60	8.31	22.26	6.40	1.42
70	9.68	18.62	7.42	1.22
80	10.96	10.95	10.23	1.13
90	12.19	5.351	23.60	1.26

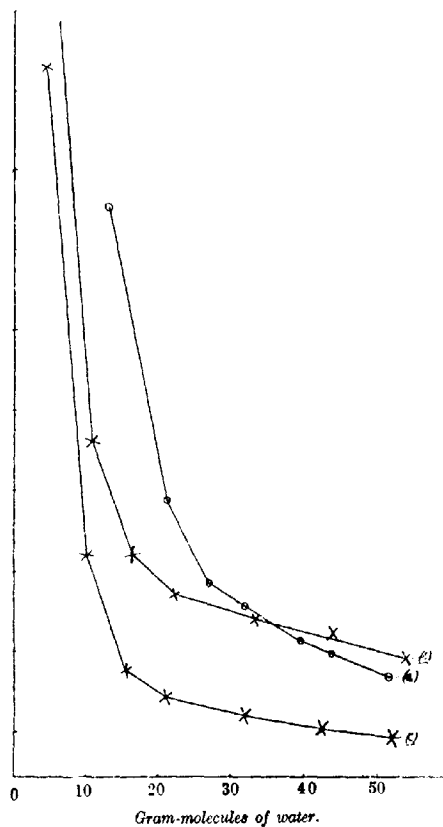
Discussion of Results.

If the values of k_1 given in tables III and IV are plotted against water concentrations, they are found to lie on a rectangular hyperbola. In the accompanying diagram, a graph is also shown for the results obtained for sucrose inversion given under k_1 in the table at the beginning of this paper. It will be seen that the three curves are similar in shape and indicate the decrease in catalytic activity of the acid which accompanies an increase in the water concentration.

Snethlage (*Zeitsch. physikal. Chem.*, 1913, **85**, 253), Acree (*Amer. Chem. J.*, 1912, **48**, 352), and Taylor (*Zeitsch. Elektrochem.*, 1914, **20**, 201) have advanced the theory that the undissociated molecule of the acid also acts as a catalyst, the activity of the undissociated molecule of hydrochloric acid varying for different reactions up to a value twice that of the hydrogen ion. In order to account for the present results according to this theory,

it would be necessary to assume that $\frac{k_m}{k_H}$ is about 20 (k_m being the activity of the undissociated molecule and k_H that of the hydrogen ion). Figures are not available for the degree of dissociation of hydrochloric acid in water-acetone mixtures, but in discussing the results obtained for the inversion of sucrose (*loc. cit.*), the author

gave values of a (HCl) deduced for water-alcohol mixtures. In the following table, the values observed for k_1 for sucrose inversion



- (a) Inversion of sucrose in water-alcohol.
 (b) Hydrolysis of methyl acetate ($N/10\text{-HCl}$) in acetone-water
 (c) " " " ($N/2\text{-HCl}$) " " " " " "

(calculated as a bimolecular reaction) are compared with the total catalytic activity of the acid expressed as

$$k_m + k_H = k_H [a + 20(1 - a)],$$

the ratio $\frac{k_m}{k}$ being taken as 20.

TABLE V.

Alcohol (volume per cent.).	α (HCl).	$[\alpha + 20(1 - \alpha)]$.	$k_1 \times 10^3$.	$\frac{k_1 \times 10^3}{[\alpha + 20(1 - \alpha)]}$.
0	0.86	3.66	4.27	1.17
25	0.83	4.23	5.19	1.23
40	0.80	4.80	6.07	1.26
50	0.72	6.32	6.67	1.06
60	0.65	7.65	8.77	1.15
75	0.45	11.45	16.03	1.11

The numbers in the fifth column approximate to a constant. Although results cannot be calculated in this way for the hydrolysis of methyl acetate in water-acetone mixtures owing to lack of data, it is considered from the results obtained for k_1 in these solutions that if the value of α (HCl) were available, a similar constancy for $\frac{k_1}{\alpha + x(1 - \alpha)}$ would be obtained for a value of x in the neighbourhood of 20.

It follows from the above that the activity of the catalyst in these mixtures can best be expressed by $k_1 = k_m + k_n$, when the ratio $\frac{k_m}{k_n}$ is considered to be about 20, but this value is not supported by results obtained by Sneath and others for the catalytic effect of hydrochloric acid in other reactions.

The shape of the curves in the diagram suggests that in the mixtures investigated the variation of the activity of the acid with the water content is approximately expressed by $k_1(w + m) = n$, where m and n are constants and k_1 the observed rate of hydrolysis in a solution containing w gram-molecules of water. An equation of this type is capable of various interpretations, but taken in conjunction with the marked decrease in k_1 with increase in water concentration for low values of the latter, it indicates that the water plays a very markedly anticatalytic rôle compared with the other constituents of the solution, that is, the value of the constant m must be very small compared with w . This may be interpreted (compare Lapworth and Fitzgerald, T., 1908, 93, 2168) as being due to the conversion of active, free hydrogen ions to inactive ions by the solvent, the effect of the water in this respect being far greater than that of the acetone. Or it may be interpreted as indicating that the reactive substance in ester hydrolysis is a complex between the ester and water, which is readily dissociated by the excess of water in the solution (Griffiths and Lewis, *loc. cit.*). It may also be interpreted as representing the dissociating effect of the solvent on a complex between the ester and the catalyst, which is considered to be the reactive

substance. Such a complex may either be dissociated by the solvent into the original substances or else hydrolysed by the water into the final products of hydrolysis. For the concentrations usually employed in hydrolysis the amount of this complex is very small owing to the high dissociating power of the water. As the latter is replaced by acetone or other liquid the dissociating power of the medium is decreased and the concentration of the complex is increased, so that the observed rate of hydrolysis is also increased. In any of the above cases it is possible to assign a small value to the term m , which really represents the relatively small power of the other constituents of the solution of converting an active substance into one which is inactive in catalysis. The following discussion is independent of the nature of m ; it is concerned rather with its magnitude. We will assume that it is simply a function of the concentration of the other variable in the solution, namely, acetone. If we substitute in the equation $k_1(w + m) = n$ the values of k_1 and w in table III for solutions containing (a) 52.32 gram-molecules of water and no acetone, and (b) 4.752 gram-molecules of water and 11.84 of acetone, we obtain the value $m = 0.22$ (in terms of 1 gram-molecule of acetone in the solution). Substituting this value for the other solutions, the following results are obtained.

TABLE VI.

Acetone.	Acetone $\times 0.22$	w .	$k_1 \times 10^4$.	$n = k_1(w + 0.22 \times \text{acetone})$.
0.0	—	52.32	2.76	144
2.665	0.59	42.46	3.03	130
5.39	1.19	32.08	3.38	112
8.10	1.78	21.23	3.86	89
9.42	2.07	15.72	4.56	81
10.66	2.35	10.20	7.40	93
11.84	2.60	4.752	19.56	144

The numbers in the last column pass through a minimum value and vary in a similar manner to the values under k in table III. Furthermore, for any small value of m in the equation $k_1(w + m) = n$, the values of n will be found to vary as in table VI. The similarity between the variations of k in table III and n in table VI appears to justify the use of the equation for a unimolecular reaction in mixtures such as those used in this work, in which the total concentration of water varies considerably in the different solutions. It would appear that any specific effect of the solvent on the rate of hydrolysis, other than that due to its dissociating power, is more directly shown by disregarding the change in the concentration of the water in the different solutions. It is considered that the minimum value obtained for k (or n) has a definite meaning. It is interpreted as indicating a specific influence of these mixtures on the rate of catalysis, similar to that

observed in the conductivity of certain electrolytes dissolved in them, or in the fluidity of the mixtures themselves. The solution of either alcohol or acetone in water is accompanied by contraction, and it is considered that the condensed state of such a mixture has a retarding influence on catalysis.

Summary.

The rates of hydrolysis of methyl acetate by $N/2$ - and $N/10$ -hydrochloric acid have been measured in various water-acetone mixtures. The velocity constants have been calculated according to both unimolecular and bimolecular equations, the reverse reactions being considered in both cases.

It has been found that if the total water concentration is taken as representing its active mass, then the rate of hydrolysis increases as water is decreased in the mixtures throughout the series. The results obtained approximate to $k_1 = k_m + k_H$ if $\frac{k_m}{k_H}$ is taken as 20 (approximately). The variation of k_1 with water concentration indicates the anticatalytic function of the latter, and if the values of k_1 are corrected for this effect the numbers so obtained are found to vary in a manner similar to those obtained by using the ordinary unimolecular equation, and pass through a minimum value for a certain mixture. This minimum is considered to have a definite meaning, representing a retarding influence of such mixtures on catalytic reactions.

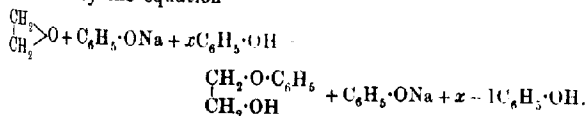
CHEMICAL LABORATORY,
UNIVERSITY OF SYDNEY.

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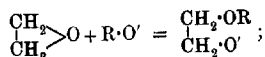
CXIV.—*The Velocities of Combination of Sodium Derivatives of Phenols with Olefine Oxides.* Part II.

By DAVID RUNCIMAN BOYD and MISS DORIS FELTHAM THOMAS.

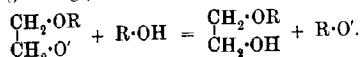
A PREVIOUS communication (Boyd and Marle, T., 1914, 105, 2117) contained an account of experiments on the combination of ethylene and propylene oxides with the sodium derivatives of a variety of phenols. The nature of the reaction investigated is indicated by the equation



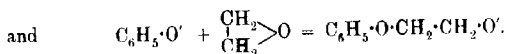
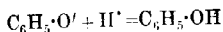
From the results of these experiments, the conclusion was drawn that combination probably, in the first instance, takes place between the phenoxy-ion and the olefine oxide molecule, thus:



the initial additive product afterwards reacting with the excess of phenol to give a glycol aryl ether and a new phenoxy-ion,



A comparison of the values for the velocity constant of the reaction with different phenols indicated that the speed of combination diminished with increase in the acidity of the phenol, and the suggestion was made that a certain analogy exists between the two reactions



In other words, where the tendency for a phenoxy-ion to change into undissociated phenol is great, the speed of combination of the phenoxy-ion with the ethylene oxide molecule should be relatively high, and vice versa. The data available at the time, however, with regard to the relative acidities of different phenols were comparatively few.

An investigation of the extent to which the sodium derivatives of alkyl substituted phenols are hydrolysed in aqueous solution was afterwards carried out by one of us (T., 1915, 107, 1538), and it then became possible to consider in more detail the relationship existing between the acidity of a phenol and the speed with which its sodium derivative combines with ethylene oxide. As a result, certain regularities with regard to the behaviour of ortho-substituted phenols came to light, and it appeared desirable to extend the observations so as to confirm, if possible, the generalisations which had suggested themselves. The present paper therefore includes experimental data for the velocity constants of three additional alkyl substituted phenols, namely, *o*-4-xyleneol, *m*-6-xyleneol, and mesitol. In all, results for eighteen phenols are dealt with. The facts are summarised in the accompanying diagram, where the velocity constants for the ethylene oxide reaction are plotted against the values for the percentage of hydrolysis of the sodium phenoxides in aqueous solution. A reference to this diagram will show that the velocity constants for phenol and

its *meta*- and *para*-substitution products lie approximately along a straight line, whilst the constants for the alkyl substituted phenols containing one alkyl group in an *ortho*-position lie approximately on a second straight line which runs nearly parallel with the first and some distance below it.

It appears, therefore, that whilst in general the speed of the ethylene oxide reaction increases approximately in proportion to the degree of hydrolysis of the sodium phenoxide, a retarding influence makes itself felt in those cases where an *ortho*-placed alkyl group is present in the phenol molecule. This retarding influence, it will be observed, is superimposed on the factor which in the main determines the speed of the reaction. It becomes apparent only as the result of such an analysis of the phenomena as is here suggested. A comparison of the actual magnitude of the velocity constant for phenol with that of the constant for any of the alkyl *ortho*-substituted phenols reveals no such retardation. Thus thymol, in the molecule of which an *isopropyl* radicle is present in the *ortho*-position to the hydroxyl group, has a velocity constant one and a half times as great as that of phenol. Mesityl, with two *ortho*-placed methyl groups, has a constant nearly twice as great as that of phenol. None the less, the retarding influence of the *ortho*-placed alkyl groups is operating in both instances. The case of mesitol is of particular interest in this connexion. Since in mesitol two *ortho*-placed methyl groups occur, the retardation might be expected to be more pronounced than in cases where only one such group is present. A consideration of the diagram shows that this anticipation is fully borne out by the experimental results.

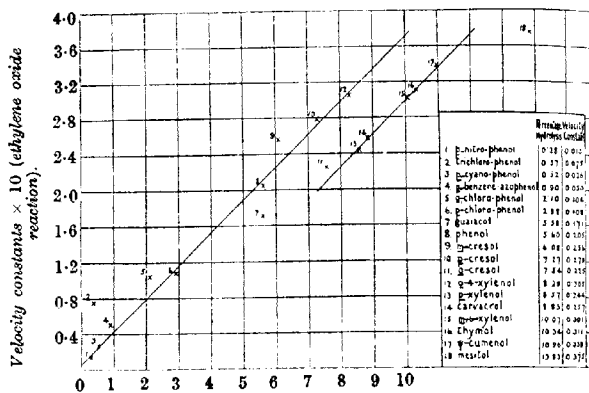
On the other hand, the position of the *o*-chlorophenol constant, and more especially of that for 2:4:6-trichlorophenol, indicates that negative substituents—or at least chlorine atoms—in the *ortho*-position act in an exactly opposite way, the velocity of combination being accelerated by their presence; and it is noteworthy that just as two *ortho*-placed alkyl groups cause a very pronounced retardation of the speed, so two *ortho*-placed chlorine atoms have an accelerating effect much more powerful than that due to a single chlorine atom.

Whilst it is natural to attribute to steric hindrance the retarding influence of the *ortho*-placed alkyl groups, a final decision on the question is not yet possible in view of the quite different effect produced by *ortho*-situated chlorine atoms. Further experimental evidence is also required to decide whether the accelerating influence of the chlorine atom should be ascribed to its residual affinity or to its polar quality. In the meantime, it may be pointed out that in the case of guaiacol, which contains an *ortho*-

situated group of ill-defined polar character, the velocity constant lies some distance above the line for phenols containing ortho-groups of well-marked positive type.

EXPERIMENTAL.

The velocity constants for *o*-4-xyleneol, *m*-6-xyleneol, and mesitol were determined at 70.4° in 98 per cent. alcohol according to the method previously described (T., 1914, 105, 2117). It was found necessary to employ a mixture of light petroleum with ether (1:1) in separating glycol *m*-6-xyleneol ether from unchanged *m*-6-xyleneol, since this phenol is not completely extracted from an ethereal



Percentage hydrolysis of sodium phenoxides in aqueous solution at 25°.

solution by repeated shaking with aqueous potassium hydroxide. The same method had to be employed in the case of the mesityl ether.

Summary of Results.

	Percentage yield of glycol ether.			$\frac{1}{t} \log \frac{100}{100-x}$
<i>o</i> -4-Xyleneol.	2 hours.	1 hour.	Maximum.	
	75.3	51.0	98.5	0.3050
<i>m</i> -6-Xyleneol.	75.1	—	—	—
	2 hours.	1½ hours.	Maximum.	
	74.5	58.5	98.9	0.3005
Mesitol.	74.8	—	—	—
	2 hours.	—	Maximum.	
	82.3	—	99.0	0.3745
	81.8	—	—	—
	82.5	—	—	—

Glycol o-xylyl ether, $C_8H_9 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, is a colourless oil boiling at $159^\circ/18$ mm. Its *p*-nitrobenzoate crystallises from alcohol in pale yellow plates melting at 225° :

0.1518 gave 6.5 c.c. N_2 (moist) at 23° and 762 mm. $N=4.82$.

$C_{17}H_{17}O_3N$ requires $N=4.62$ per cent

Glycol m-xylyl ether, $C_8H_9 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, was obtained as a white solid, which, after recrystallisation from light petroleum, melted at 57° :

0.1621 gave 0.4289 CO_2 and 0.1252 H_2O . $C=72.16$; $H=8.58$.

$C_{10}H_{14}O_2$ requires $C=72.23$; $H=8.51$ per cent.

Glycol mesityl ether, $C_9H_{11} \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, separates from light petroleum in glistening, white crystals which melt at 60° :

0.1556 gave 0.4196 CO_2 and 0.1263 H_2O . $C=73.54$; $H=9.02$.

$C_{11}H_{16}O_2$ requires $C=73.25$; $H=8.97$ per cent.

THE UNIVERSITY COLLEGE
OF SOUTHAMPTON.

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(XV.—Molecular Refractivity of Cinnamic Acid Derivatives.

By ERIC WALKER and THOMAS CAMPBELL JAMES.

THE work of previous investigators has shown that the molecular refractivity of organic compounds is affected to a slight extent by constitutive influences within the molecule. In this investigation we have determined the amount of variation produced by change of constitution in a series of closely allied derivatives of cinnamic acid, and the results are tabulated below:

	[M] ₁ .	Difference.	[M] ₂ .	Difference.
<i>a</i> -Chlorocinnamic acid	50.24	—	50.96	—
<i>a</i> -Chloro <i>allo</i> cinnamic acid	49.00	1.24	49.59	1.37
Ethyl <i>a</i> -chlorocinnamate	58.33	—	58.98	—
Ethyl <i>a</i> -chloro <i>allo</i> cinnamate...	57.61	0.72	58.19	0.79
<i>a</i> -Bromocinnamic acid	52.90	—	53.52	—
<i>a</i> -Bromo <i>allo</i> cinnamic acid	52.34	0.56	53.06	0.46
Ethyl <i>a</i> -bromocinnamate	60.85	—	61.51	—
Ethyl <i>a</i> -bromo <i>allo</i> cinnamate...	60.54	0.31	61.14	0.37
<i>a</i> -Bromocinnamic acid	51.98	—	52.61	—
<i>a</i> -Bromo <i>allo</i> cinnamic acid ...	51.53	0.45	52.10	0.51
Dibromocinnamic acid	58.94	—	59.64	—
Dibromo <i>allo</i> cinnamic acid ...	—	—	—	—
Allyl <i>a</i> -chlorocinnamate.....	62.13	—	62.82	—
Allyl <i>a</i> -chloro <i>allo</i> cinnamate ...	60.52	1.61	61.08	1.74

An examination of the above figures confirms Brühl's observation that the more stable isomeride has the higher molecular refractivity, and shows also that, in the α -substituted compounds the difference decreases with increase of molecular weight. It is also seen, from a consideration of the bromo-acids, that the α -substituted acid has a greater refractive power than the β -substituted acid.

EXPERIMENTAL.

(a) *Refractivity Measurements.*

Materials.—The acids and esters used in this investigation were all specially prepared, and the greatest care was taken to use only highly purified specimens for refractivity measurements. Details of new preparations are given at the end of the paper.

The solvent used for the acids was ethyl alcohol, rendered absolute by distilling the 99.8 per cent. commercial product over lime and afterwards over metallic calcium.

Apparatus and Method.—The solutions of the acids were made up by direct weighing to determine their percentage composition. In all cases, approximately 5 per cent. solutions were employed. The esters were all liquids and were determined directly.

Densities were determined by means of a Sprengel-Ostwald pyknometer of about 5 c.c. capacity. The pyknometer was suspended in a thermostat kept at 25° ($\pm 0.05^{\circ}$) for about fifteen minutes. The following formula was used:

$$d_4^{25} = \frac{W'D}{W} - 0.0012 \frac{(W' - W)}{W},$$

where d_4^{25} = density of solution at 25° , referred to water at 4° ,

W' = weight of solution filling pyknometer,

W = weight of water filling pyknometer,

D = density of water at 25° (0.997073).

Refractive indices were measured by means of a form of Pufrich refractometer furnished with an ordinary thermostat. The temperature of the liquid in the cell could be maintained at 25° ($\pm 0.05^{\circ}$) for a considerable time.

The refractive index of each liquid was measured for the C and D lines.

The zero error of the refractometer amounted to $+1'$, and all readings were corrected for this. The temperature correction amounted to about one unit in the fifth place of decimals in the refractive index, and could therefore be neglected.

The refractive index of the alcohol used as solvent was deter-

mined several times during the course of the work. The following values were obtained:

$$n_c = 1.35787, 1.35784, 1.35774.$$

$$n_D = 1.35967, 1.35967, 1.35954.$$

The specific refractivity, r , of the solute was calculated by the formula

$$r = \begin{bmatrix} \frac{n^2-1}{n^2+2} & \frac{1}{d} & \frac{100}{p} \end{bmatrix} - \begin{bmatrix} \frac{n_a^2-1}{n_a^2+2} & \frac{1}{d} & \frac{100-p}{p} \end{bmatrix},$$

where n and d are refractive index and density of the solution at 25° , n_a and d_a are the corresponding quantities for alcohol at 25° , and p is the percentage composition by weight of solution.

For the pure esters the formula

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$$

as employed.

In the tables which follow, p and d have the same significance as above, n_C and n_D denote the indices of refraction for the C and D lines respectively, r_C and r_D refer to the specific refractions, and M_C and $[M]_D$ to the molecular refractions for these lines. In the column headed "solution," the number refers to the specimen of substance used, whilst the letters denote the various solutions made up from the same specimen.

TABLE I.

α -Bromocinnamic Acid.

Constants for alcohol: $d=0.7851$; $n_c=1.35787$; $n_D=1.35967$.

Solution.	p .	d .	n_1 .	n_{10} .	τ_1 .	τ_{10} .	[M] ₁ .	[M] ₁₀ .
a	5-041	0-8069	1-36552	1-36742	0-2332	0-2351	52-94	53-37
b	5-192	0-8076	1-36580	1-36780	0-2332	0-2364	52-94	53-66
b	4-677	0-8053	1-36493	1-36691	0-2327	0-2358	52-83	53-53
					Means	...	52-90	53-52

TABLE II.

α -Bromoallocinnamic Acid.

Constants for alcohol as in table I.

la	5.330	0.8077	1.36555	1.36757	0.2310	0.2342	52.43	53.18
lb	4.824	0.8056	1.36483	1.36681	0.2304	0.2338	52.30	53.07
lc	5.248	0.8075	1.36547	1.36747	0.2304	0.2333	52.30	52.96
						Means ...	52.34	53.06

TABLE III.

 α -Chlorocinnamic Acid.

Constants for alcohol as in table I.

Solution.	<i>p</i> .	<i>d</i> .	<i>n_c</i> .	<i>n_D</i> .	<i>r_c</i> .	<i>r_D</i> .	[M] _c .	[M] _D .
1a	5.190	0.8034	1.36686	1.36893	0.2754	0.2795	50.26	51.01
1b	4.984	0.8026	1.36645	1.36851	0.2751	0.2793	50.20	50.97
1c	5.136	0.8031	1.36873	1.36879	0.2755	0.2796	50.28	51.03
2a	5.469	0.8042	1.36724	1.36930	0.2751	0.2785	50.21	50.83
Means ...							50.24	50.96

TABLE IV.

 *α -Chloroalloeinnamic Acid.*Constants for alcohol: *d*=0.7851; *n_c*=1.35774; *n_D*=1.35954.

1a	5.008	0.8021	1.36560	1.36758	0.2685	0.2716	49.00	49.57
1b	5.051	0.8024	1.36570	1.36767	0.2681	0.2711	48.93	49.48
2a	5.206	0.8024	1.36576	1.36776	0.2689	0.2725	49.07	49.73
Means ...							49.00	49.59

TABLE V.

 β -Bromocinnamic Acid.

Constants for alcohol as in table IV.

1a	4.877	0.8062	1.36489	1.36681	0.2296	0.2317	52.12	52.60
2a	4.512	0.8045	1.36426	1.36623	0.2284	0.2318	51.85	52.62
Means ...							51.98	52.61

TABLE VI.

 β -Bromoalloeinnamic Acid.

Constants for alcohol as in table IV.

1a	5.044	0.8061	1.36454	1.36649	0.2270	0.2295	51.53	52.10
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TABLE VII.

Dibromocinnamic Acid.

Constants for alcohol as in table IV.

1a	5.205	0.8107	1.36412	1.36603	0.1926	0.1949	58.94	59.64
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TABLE VIII.

Ethyl α -Chlorocinnamate.

<i>d</i> .	<i>n_c</i> .	<i>n_D</i> .	<i>r_c</i> .	<i>r_D</i> .	[M] _c .	[M] _D .
1.1719	1.56292	1.57054	0.2771	0.2802	58.33	58.98

TABLE IX.

Ethyl α -Chloroalloeinnamate.

1.1569	1.54597	1.55246	0.2737	0.2764	57.61	58.19
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TABLE X.

Ethyl α -Bromocinnamate.

<i>d.</i>	<i>n_D</i>	<i>n_D²⁰</i>	<i>r_D</i>	<i>r_D²⁰</i>	[M] _D ²⁵	[M] _D ²⁰
1.3885	1.57685	1.58450	0.2386	0.2412	60.85	61.61

TABLE XI.

Ethyl α -Bromallocinnamate.

1.3713	1.56474	1.56973	0.2374	0.2398	60.54	61.14
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TABLE XII.

Allyl α -Chlorocinnamate.

1.1702	1.56718	1.57483	0.2792	0.2823	62.13	62.82
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TABLE XIII.

Allyl α -Chloroallocinnamate.

1.1457	1.53563	1.54164	0.2720	0.2745	60.52	61.08
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Preparations.

Ethyl α -chlorocinnamate, $C_6H_5 \cdot CH:CCl \cdot CO_2 \cdot C_2H_5$.

B. p. 161—162°/8 mm. D_4^{25} 1.172.

0.3467 required 1.621 c.c. *N*-AgNO₃. Cl=16.60.

$C_{11}H_{11}O_2Cl$ requires Cl=16.84 per cent.

Ethyl α -chloroallocinnamate.

B. p. 157—158°/10 mm. D_4^{25} 1.157.

0.2985 required 1.392 c.c. *N*-AgNO₃. Cl=16.54.

$C_{11}H_{11}O_2Cl$ requires Cl=16.84 per cent.

Allyl α -chlorocinnamate, $C_6H_5 \cdot CH:CCl \cdot CO_2 \cdot CH_2 \cdot CH:CH_2$.

B. p. 162—163°/11 mm. D_4^{25} 1.170.

0.3340 required 1.470 c.c. *N*-AgNO₃. Cl=15.61.

$C_{12}H_{11}O_2Cl$ requires Cl=15.93 per cent.

Allyl α -chloroallocinnamate.

B. p. 171°/28 mm. D^{25} 1.146.

0.2841 required 1.258 c.c. *N*-AgNO₃. Cl=15.70.

$C_{12}H_{11}O_2Cl$ requires Cl=15.93 per cent.

From the above, it will be observed that the boiling points and densities of the *allo*-esters are always below those of the *trans*-*ortho*.

THE EDWARD DAVIES CHEMICAL LABORATORIES,

ABERYSTWYTH.

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CXVI.—*The Determination of Ignition-temperatures
by the Soap-bubble Method.*

By ALBERT GREVILLE WHITE and TUDOR WILLIAMS PRICE.

THE soap-bubble method for the determination of ignition-temperatures was first described by McDavid (T., 1917, 111, 1003). In the method as finally adopted, the experimental error is assumed to be less than $\pm 3^\circ$, and the results obtained for the ignition-temperatures of the various gases tested are given as:

Coal gas-air	878°
Ethylene-air	1000
Hydrogen-air	747
Carbon monoxide-air	931
Petrol (fraction 0–80°)-air	995
Benzene-air	1062
Ether-air	1033

The method is said to eliminate, so far as is practically possible, the time factor. The temperature of ignition is taken to be that temperature to which the gaseous mixture must be heated by the application of a hot body, so as to cause instantaneous ignition. McDavid's results are very high in comparison with other recent determinations.

Finding it necessary to determine the ignition-temperatures of certain ether-air mixtures, the authors decided to use the apparatus described by McDavid on p. 1005 (*loc. cit.*).

The igniting coil was mounted between two binding screws fixed into a small wooden stand, and was kept at the requisite temperature by means of current drawn from a battery of accumulators. A variable resistance of nichrome ribbon formed part of the circuit, which was completed by means of a sliding contact-maker. The current was measured by means of a delicate ammeter reading to 0.01 ampere. The soap solution was prepared by dissolving sodium oleate in water with the addition of a little glycerol. In all the experiments in which ether was used the ether-air mixture was made by weighing the requisite quantity of ether into an exhausted aspirator, from which it was displaced later by means of mercury. It was found that the presence of mercury caused a slight change in the concentration of the solvent above it. The glass pipe from which the bubbles were blown was connected to the aspirator by means of a ground-glass joint, so that there was no possibility of change in the concentration of the ether due to absorption of the vapour by the leading tube, which was of glass. In the other experiments the vapour-air mixture was

made by weighing the requisite amount of liquid into an exhausted 15-litre aspirator, and was in this case displaced by means of water. The hydrogen-air mixture was made up by volume in the same apparatus.

Standardisation of Apparatus.

The coils were standardised as described by McDavid; the salts used were carefully purified and were kept in an exhausted desiccator over phosphoric oxide. Before use the salt was crushed and only minute fragments were placed on the coil. When these precautions were taken the standardisation could almost invariably be repeated to 0.01 ampere. The number of amperes necessary to keep the coil at such a temperature, that, when in a steady state, the salt was just melted, was taken to be the amperage necessary to heat the coil to the melting point of that salt. The melting points are given in table I, and are the same as given by McDavid, except in the case of lead chloride, which he did not use.

TABLE I.

Salt employed.	Melting point used.	Melting point given in "Chemist's Year Book" for 1916.
Potassium sulphate.....	1072°	1050°
Sodium chloride	800	820
Potassium iodide.....	687	705
Lead chloride	485	485

For comparison the figures supplied in the "Chemist's Year Book" for 1916 are given. It will be seen that the difference between these and the figures used is by no means negligible; the figure for lead chloride was taken from this source. Every effort was made to wind the coils as uniformly as possible, but in almost every case it was found that patches rather hotter than the average could be found.

In Fig. 1 are given the standardisations of some of the coils. It will be noticed that these curves are not straight lines, as was that determined by McDavid in the case of the coil used by him, but have a distinct curvature.

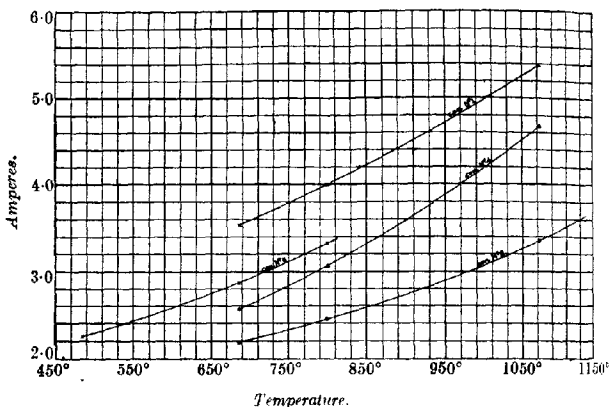
Standardisation of the Method.

Little work appears to have been done as regards standardising the soap-bubble method. McDavid used a soap-bubble 3.7 cm. in diameter, but no figures are given showing the effect of the size

of the bubble, or the place or the method of striking. All the standardisation undertaken in connexion with this method was done with coil No. 1, and most of it was carried out with ether-air mixtures, although in some cases hydrogen-air mixtures were also used, similar results being obtained. Throughout the work an attempt was made to keep the room temperature within 2° of 18° . For some time it was found exceedingly difficult to obtain accurate and steady ammeter readings, but the erection of a draught screen round the apparatus, and the gradual elimination of poor connexions, remedied these faults. It was also found that owing to the comparatively high currents used, the nichrome resistance

FIG. 1.

Showing the standardisation curves connecting the ammeter reading and temperature for various coils.



required frequent cleaning, and that the sliding contact-maker had to be silvered or fitted with a platinum contact.

So far as could be judged from the steadiness of the ammeter reading, no appreciable change in the temperature of any coil took place when it was brought into contact with a soap bubble blown with air. When using platinum-wound coils at the temperature necessary for the experiments, a very slight draught caused a distinct rise in the ammeter reading.

When determining an ignition-temperature the amperage was taken at which at least two ignitions were obtained out of three attempts, whilst 0.01 ampere below at least three successive failures to ignite were registered.

Size of Bubble and Place of Striking.

It was found that the size of the bubble used, and the place of striking, affected the results very appreciably, and various experiments were carried out in order to determine the magnitude of the variations due to these factors. The results of some of these tests are given in table II.

TABLE II.

Position of striking surface on bubble.	Mixture containing 7.5 per cent. of ether in air. Number of amperes necessary to ignite.			Mixture containing 12.5 per cent. of ether in air. Number of amperes necessary to ignite.		
	2.5 cm. bubble.	3.7 cm. bubble.	5 cm. bubble.	2.5 cm. bubble.	3.7 cm. bubble.	5 cm. bubble.
Struck at top	5.29	5.05	5.02	5.31	5.20	5.18
Struck at middle ...	5.29	5.05	5.02	5.32	5.20	5.18
Struck at bottom ...	5.41	5.08	5.03	5.43	5.22	5.20

On plotting the above results graphically, as in Fig. 2, it will be seen that the correct result appears to be about 0.01 ampere below the current necessary for the ignition of a 5 cm. bubble. Similar results were obtained using other concentrations of ether vapour in air. It scarcely appears to matter whether the bubble is struck at the top or middle, but striking at the bottom invariably gives a lower result. In practice, bubbles were always struck as near the middle as possible, and a 5 cm. bubble was always used. This size of bubble gave some little trouble owing to a tendency to give delayed ignitions and to burst before use, both effects being particularly noticeable with mixtures containing much ether. There was also a great tendency for the ether to leak through these bubbles. The method of striking was also found to have a great influence on the result, but it was found that a slow, but not too slow, approach of the coil to the bubble, or, even better, of the bubble to the coil, gave very consistent results. When the approach of the bubble was too slow, the ether pouring out through the soap film heated the coil so that the ammeter reading did not register its correct temperature.

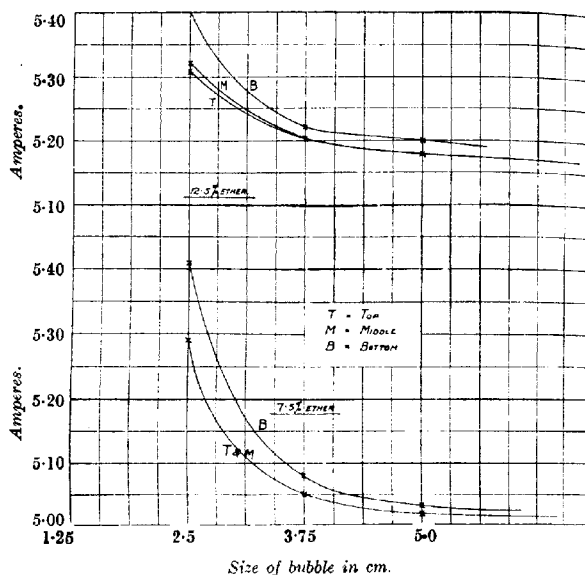
Time between Ignitions.

It was also found that a fair time had to elapse after one ignition before another could be attempted with any certainty of obtaining a trustworthy result. Even if a bubble was not ignited, heating of the coil took place, and a second bubble was very often

ignited at what was apparently the same temperature, unless time were given for the coil to cool. At least one minute had to be allowed between each attempted ignition, and often a longer time was necessary, the interval varying from coil to coil. It was also found that the time necessary for an adjustment of temperature

FIG. 2.

Showing how the current necessary to ignite a definite mixture varies with the size of bubble and position of striking.



due to change in the magnitude of the current flowing, varied greatly from coil to coil.

Changes in the Coil.

Even when experiments were carried out precisely as described in the above method, it was found that a coil gave different results for the same combustible mixture, even on the same day. Careful observation showed that these variations were generally all in one direction, and a connexion was soon traced between them and the standardisation of the coil used.

In table III are given the ignition-temperatures of a 4.9 per

ent. ether-air mixture determined with coil No. 1 at various times after standardisation.

TABLE III.

Within 20 minutes. 968°	After 3 days' use. 985°	After 3 weeks' use. 1040°	20 Minutes after re-standardising. 970°
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It will be seen at once that the addition of salts to coil No. 1 lowered the ignition-temperature of the ether-air mixture as given by this method by 70°. Some such change might have been anticipated from the later work of Meunier (*Compt. rend.*, 1909, **149**, 124; 1910, **150**, 781). That this was not due to a change in the resistance of the coil can be seen from the fact that throughout the six months during which this coil was in use no point on the standardisation curve varied throughout a range of more than 0.02 ampere except on one occasion, when a variation of 0.03 was found. Precisely similar results were obtained in a test experiment on standardisation, even without washing off the salts used, as was invariably done in practice. A further investigation was then undertaken in order to discover how the ignition-temperature of a particular mixture varied with the treatment to which the coil was subjected.

The ammeter readings taken when using the untreated coil were converted into temperatures after the coil had been standardised by the use of salts. This was considered legitimate as every precaution was taken to ensure that the current-temperature ratio of the coil did not change with use. It was found that the newly-wound coil gave ignition at ammeter readings which increased continuously with time up to a steady value. The first ignition-temperature determined for a 27 per cent. hydrogen-air mixture, using coil No. 2 before treatment, was 760°. In a week's time the ignition-temperature had increased to 860°, but after this time no appreciable change in ammeter reading could be detected.

After standardisation or using salts it was found that a decided rise in the ignition-temperature had always taken place. This was invariably followed by an initially rapid fall, which decreased until a steady state was reached, the rate of decrease of temperature varying considerably with the nature of the coil, and its previous treatment. Thus, an untreated wire would take a very much longer time to reach a steady state than a recently treated or even a well washed wire which had once reached that state. For instance, the ignition-temperature of an ether-air mixture as determined by means of a platinum coil treated for the first time would probably take several days to become constant, whereas in

the case of a recently treated coil twenty minutes would be ample time.

Two hours after coil No. 2 was first treated with salts, the ignition-temperature of a 5 per cent. ether-air mixture as registered by this coil had fallen from 1068° to 1019° , whilst that of a 12 per cent. mixture, after its preliminary rise from 986° , had fallen to 1006° (see table IV). In both these cases the ignition-temperature of a 5 per cent. ether-air mixture appears to have fallen much more rapidly than that of a 12 per cent. mixture, as would be expected from the curves shown in Fig. 5.

In order to maintain a coil in the steady state, it was necessary to treat with salts occasionally. This caused a temporary rise in ignition-temperature, but it was only a matter of minutes before the steady state was re-established. The manner in which the ignition-temperature changed when no salts were added to a coil in the steady state can be seen from table III.

The temperature at which a steady state was attained after treatment was greater than without treatment except in the case of coils 1 and 2, which were of platinum. The variation was complicated in the case of the nichrome coil No. 3 by the fact that after being in the steady state for three days with a fairly continuous treatment with salts, a rather rapid fall in ignition-temperature became evident. When the fall became slower, the two points shown by asterisks in Fig. 5 were obtained, the one value, for a 5 per cent. ether-air mixture, being the mean of two readings 0.04 ampere apart obtained before and after the determination for a 12 per cent. ether-air mixture.

It will be noticed that in this case the ignition-temperature of a 5 per cent. ether-air mixture has fallen much more rapidly than that of a 12.5 per cent. mixture. This experiment was unfortunately interrupted by the breaking of the silica tube on which the coil was wound, making it impossible for the experiment to be carried to its logical conclusion; but it is at least possible that a flattened curve well below the original one (without salts) would have been obtained here as in the case of No. 1.

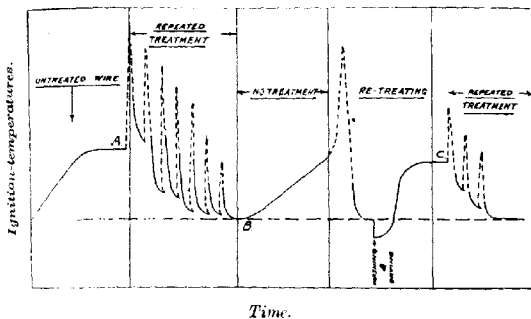
The upward change shown in table III could be made to take place even faster if the salts were washed from the coil and the coil used without treatment after drying. It was found that after eighteen hours' soaking of the coil in water, the ignition-temperature of a 27 per cent. hydrogen-air mixture as indicated by coil No. 1 fell from 787° to 771° and that of a benzene-air mixture fell from 1060° to 1056° . After sixty hours' soaking the result obtained for the hydrogen-air mixture was 773° and that for the benzene-air mixture 1056° . In all the above cases the ignition-

temperature was determined immediately after the drying of the coil was complete. During the course of three days after this preliminary fall, ignition-temperatures determined by this coil continued to rise, and at the end of this time, when the rise had become very slow, the figure found for the hydrogen-air mixture was 793° and that for the benzene-air mixture 1075° . Further results of a similar kind will be found later.

The effects of the changes considered above are shown in Fig. 3. It will be seen that consistent results are only to be expected under conditions corresponding with the three portions of the curve marked A, B, and C. Except where otherwise stated, results detailed later correspond with these steady states.

FIG. 3.

Showing diagrammatically the effect of various changes during the treatment of the wire on the ignition-temperatures registered by a coil.



Influence of the Material of the Coil.

McDavid (*loc. cit.*) states that the ignition-temperature of a 90 per cent. hydrogen-air mixture as determined by a Eureka wire coil is 9° to 30° lower than that obtained with platinum wire, and the statement is made that "The figures found by using platinum are higher than those obtained by using Eureka wire, indicating a catalysing effect in the case of the latter. It is, however, probable that both substances exert a catalytic influence." The results given above for coils Nos. 1 and 2 make it certain that the temperatures obtained are influenced very greatly by surface action in every case. It was accordingly decided to determine the ignition-temperatures of various ether-air mixtures using coils of different materials.

Coil No. 1 was made by winding platinum wire, 0.038 cm. in diameter, round a notched strip of mica.

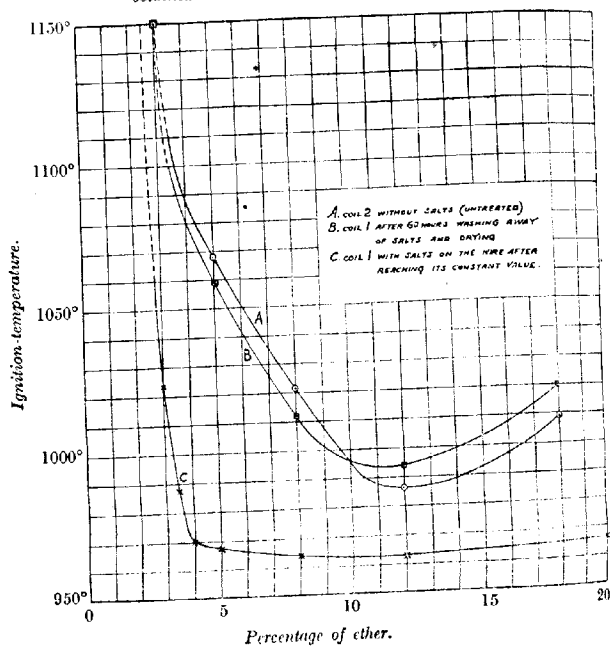
Coil No. 2 was a similar coil made with platinum wire, 0.025 cm. in diameter.

Coils Nos. 3 and 4 were made by winding nichrome wire, 0.05 cm. in diameter, round a narrow silica tube.

Coil No. 5 consisted of platinum wire, 0.025 cm. in diameter,

FIG. 4.

Showing the ignition-temperatures of various ether-air mixtures obtained with coils of platinum wire wound on mica.



wound inside a silica tube and having the platinum leads shielded by tubes of silica.

Coil No. 6 consisted of platinum wire of the same diameter as used in coil No. 5 enclosed in a uniform hard-glass tube with the leads safeguarded as for coil No. 5.

Fig. 4 gives the ignition-temperature curves obtained by plotting the results for various ether-air mixtures determined by means of

coils Nos. 1 and 2. It will be noticed that the curve obtained when coil No. 2 had attained a steady state before being treated with salts (or standardised) is close to that obtained when coil No. 1 had been allowed to attain a steady state after all the salts had been removed by prolonged washing and use. Curve *C* shows the ignition-temperatures obtained when coil No. 1 is treated with salts until the ignition-temperature obtained is constant. It differs from the other two curves inasmuch as the main body is very much flatter and that the difference in ignition-temperature between a 5 per cent. mixture and a 12 per cent. mixture of ether and air is very much less. The ignition-temperature of a 5 per cent. ether mixture as obtained from different curves on this diagram varies by 100° , whilst the maximum difference in the case of a 12 per cent. mixture is little more than 30° .

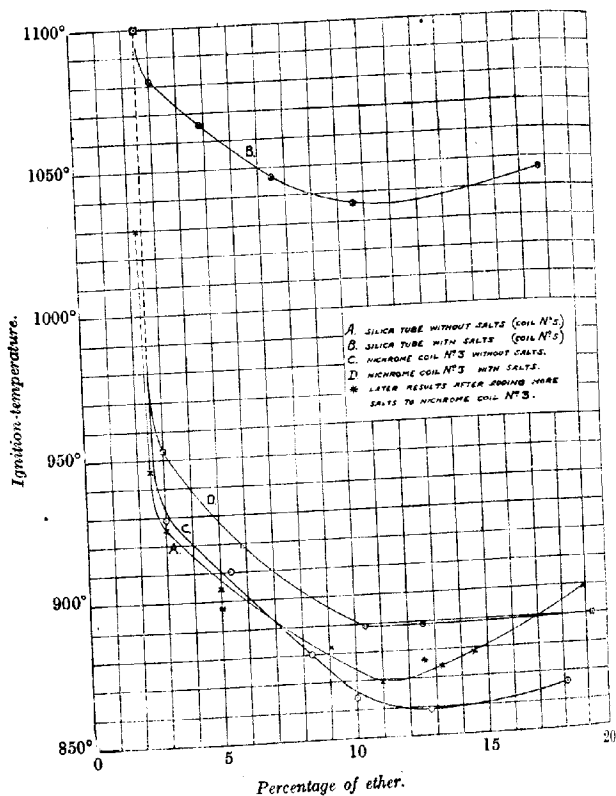
Fig. 5 gives the results obtained, using coils 3 and 5. With both these coils a more or less steady state was attained at a point above the ignition-temperature before treatment, and very much above in the case of the silica tube, No. 5. In this case, as before, the treated coils give flatter curves, and the maximum difference between the ignition-temperatures of 12 per cent. mixtures appears to be about 175° , whilst the maximum difference obtained for a 5 per cent. mixture is about 160° .

An examination of the results given in these two sets of curves shows that the ignition-temperature of any particular mixture as obtained by this method can vary very greatly. For example, the ignition-temperature of a 12 per cent. mixture of ether and air can be considered to be anything from 859° to 1035° . The explanation, of course, lies in the fact that a catalytic action—surface action—must be exerted by the coil, as would naturally be expected of any hot body inserted into a combustible gas; but it is fairly evident that the greater catalytic action is not exerted by the coil giving the lower ignition-temperature, as suggested by McDavid, but by that giving the higher. The *modus operandi* is probably as follows: When the coil is brought into the gas the combustible portion near it is at once removed by surface combustion, and this weakens the concentration of combustible gas near the coil to such an extent that it is only when the radiation from the coil is of sufficient intensity to ignite the gas outside this limited sphere that ignition occurs. This reasoning, which appears to be quite in keeping with what is known of the combustion of gases on surfaces, explains why in McDavid's experiments platinum gave a higher result than Eureka wire, and in the experiments described above, why, in the normal state, it gave results higher than either silica or nichrome when unaffected by salts. This

would also explain the reason why a coil had to be used for some time before attaining its maximum activity, as described in the standardisation of the apparatus.

FIG. 5.

Showing the ignition-temperatures of various ether-air mixtures obtained with coils of nichrome wound on silica and platinum inside silica.



Value of Method for obtaining Comparative results.

Although under any particular set of conditions the soap-bubble method is capable of giving results consistent to within $\pm 5^\circ$, it will be seen that, giving as it does, such a range for the ignition

temperature of any one gas-air mixture, it could scarcely be capable of giving the true ignition-temperature, particularly as surface action is bound to occur even when using the most indifferent material possible. It thus becomes a question as to whether even comparative results could be obtained by this method. It is seen from the curves given in Figs. 4 and 5 that those obtained with different coils occasionally cut one another, indicating that even comparative results could scarcely be obtained, assuming the experimental methods could be guaranteed accurate. As, however, the melting points of the salts used for standardisation purposes are not known to any great degree of accuracy, and the standardisation curves are not straight lines, this evidence can scarcely be regarded as final. It was therefore decided to test several combustible mixtures, using the coils already made, in order to see if comparative results could be obtained by this method. Accordingly, the following mixtures were used, in addition to those mentioned previously:

1. A mixture of 27 per cent. of hydrogen in air.
2. A mixture of 5.7 per cent. of benzene in air
3. A mixture of 0.23 gram of light petroleum (b. p. 90—100°) per litre of air.
4. A mixture of 0.23 gram of light petroleum (b. p. 60—80°) per litre of air.

It was found to be impossible to obtain a definite ignition-temperature for a mixture of carbon disulphide and air or to ignite any mixture of alcohol and air or to obtain a reasonable size of bubble with mixtures of acetone and air. The results obtained are given in table IV.

In the course of these experiments it was noticed that it was easier to obtain an accurate result with hydrogen than with any of the other gases, and it was also very obvious that coils Nos. 5 and 6 gave results sooner and more accurately than the others. With any gases examined, when using these coils, it was easy to redetermine any figure to within 0.01 ampere, whilst with the other coils twice this variation was often found. Coils Nos. 1 and 2 scarcely changed at all during six months' use, but the result was far different in the case of coils wound over silica tubing. For example, three nichrome coils had to be rejected before a coil was found which would not change on heating, and this had to be kept at an exceedingly high temperature for some time before it reached this constant state. To test the comparative accuracy of the method, a second coil of platinum wound inside a hard glass tube was made and the ignition-temperature of a hydrogen-air mixture before treatment with salts determined.

TABLE IV.
Ignition temperature.

		Ignition temperature.					
		Hydrogen-air, 27 per cent.	Light petroleum (b.p. 90-100°) -air, 0.23 gram per litre.	Light petroleum (b.p. 60-80°) -air, 0.23 gram per litre.	Benzene-air, 5.7 per cent.	Ether-air, 5 per cent.	Ether-air, 12 per cent.
No. 1.	With salts	787	1035	1056	1060	968	963
	After washing and use	793	1067	1075	1075	1089	994
No. 2.	Without salts	860	1038	1040	1045	1068	986
	With salts before constant	820	1040	1055	1060	1019	1006
No. 3.	Without salts	—	—	—	—	911	859
	With salts	—	—	—	—	928	888
No. 4.	Without salts	764	1003	999	1025	—	—
	With salts	773	1025	1016	1031	—	—
No. 5.	Without salts	—	—	—	—	907	870
	With salts	—	—	—	—	1064	1035
No. 6.	Without salts	715	—	—	—	—	—
	With salts	762	—	—	—	—	—
	After washing	735	—	—	—	—	—

The result was quite satisfactory, as on standardisation it was found that the ignition-temperature obtained in this case was 712° , the result obtained using coil No. 6 being 715° . No similar tests were carried out with the other coils, as it was considered that in all cases except that in which a platinum coil was wound inside silica or glass, such a test would probably have been useless, as the ratio of the areas of the two constituent surfaces of the coil was bound to vary for every coil made. The results are interesting, as they show that the ignition-temperatures of two gaseous mixtures obtained by this method may not even be comparative when determined by two different coils. This was carefully tested in the case of the mixtures of the two varieties of light petroleum and air by using coil 4 without salts and coil 1 with salts. When coil No. 4 without salts was kept at 1001° and bubbles of the above mixtures were brought into contact with it alternately, in every case the mixture containing the light petroleum of lower boiling point ignited, whilst in only one trial out of five did the other one ignite. A similar experiment with coil No. 2 showed that the ignition-temperature of a mixture containing the light petroleum of lower boiling point was higher than that of the other as measured by this coil.

A similar result was obtained when dealing with a 5 per cent. mixture of ether in air, as in every case except when determined by coil No. 2 before treatment with salts, the ignition-temperature of this mixture was found to be lower than that of the light petroleum and benzene mixtures. In the case of the coil specified, however, the ignition-temperature found for a 5 per cent. mixture of ether in air was definitely higher than those of the other mixtures mentioned above.

In table V are given the maximum and minimum values obtained for the ignition-temperatures of certain of the mixtures used.

TABLE V.

W = Washed.			
W.S. = Without salts.			
S = After using salts.			
Mixture used.	Maximum ignition- temperature observed.	Minimum ignition- temperature observed.	Difference.
Hydrogen (27 per cent.) in air	860° Coil 2 W.S.	715° Coil 6 W.S.	145°
Light petroleum (b.p. 90 – 100°) 0.23 gram per litre in air	1067 Coil 1 W.	1003 Coil 4 W.S.	64

TABLE V. (*continued*).

Mixture used.	Maximum ignition- temperature observed.	Minimum ignition- temperature observed.	Difference.
Light petroleum (b.p. 60–80°) 0.23 gram per litre in air	1075° Coil 1 W.	999° Coil 4 W.S.	76°
Benzene (5.7 per cent.) in air	1075 Coil 1 W.	1025 Coil 4 W.S.	50
Ether (5 per cent.) in air	1068 Coil 2 W.S.	907 Coil 5 W.S.	161
Ether (12 per cent.) in air	1035 Coil 5 S.	859 Coil 3 W.S.	176

When it is considered that the glass and silica coils were only used for the hydrogen and ether mixtures respectively, it will be seen that the results have an appreciable regularity as regards what is generally considered to be the catalytic order of the various substances concerned in the ignition. In this connexion, it must not be forgotten that the substance on which a metal coil is wound must affect the ignition-temperature obtained.

A comparison of the ignition-temperatures obtained, using coil No. 2 with and without salts, is also interesting. In the case of the hydrogen-air mixture and the 5 per cent. ether-air mixture, the treated coil gives appreciably lower results than the same coil without salts, but the reverse of this is true of all the other mixtures except light petroleum (b. p. 90–100°) and air when the ignition-temperatures are practically the same in the two cases.

On summing up, it will be seen that the only advantages which the method possesses appear to be those due to its convenience and rapidity in use. It was easy to find the apparent ignition-temperature of any mixture within less than an hour, and, using coils 5 or 6, it could often be done in half that time. The term "instantaneous ignition" is obviously used by McDavid to mean ignition without perceptible delay, but refined methods of time measurement would certainly show that different retardations occurred with different gas mixtures. Its disadvantages appear to lie in the fact that, so far as can be ascertained from these experiments, it cannot give the true ignition-temperature of any gas mixture, and that the results given by it can scarcely be utilised unreservedly even when only required for comparative purposes. Such results are fairly certain to be higher than the true ignition-temperatures, and not, as described by McDavid, lower. The accuracy of the method is also adversely affected by the fact that the exact melting points of the salts used are still a matter for controversy, and that the standardisation curve for any coil appears

from these experiments unlikely to be a straight line. The results are exceedingly dependent on draughts, as the method of estimating temperature is an indirect one. If the temperature of the coil falls during an experiment, due to any such disturbance in outside conditions, the ammeter reading, and hence the temperature indicated, becomes higher instead of lower, owing to the change in resistance of the platinum or other metal forming the heating coil. Any result obtained also seems to depend on the state of the surface causing ignition, as used and unused wire give different ignition-temperatures for the same gas mixture, and an examination under a good lens of wire that has been in use for some time shows it to have altered appreciably in appearance. Amongst its other disadvantages is that of limited applicability. It can only be applied to moist gases and to those which are more or less insoluble in water and can be obtained at a fair concentration in air at the ordinary temperature. For instance, it was found impossible to ignite a mixture of amyl acetate and air, made up at 20°, by this method. Another disadvantage lies in the fact that the least concentration of combustible gas at which ignition can be obtained by the soap-bubble method is much greater than that found by ordinary methods, which generally give results below 2 per cent. for ether-air mixtures. Thus the ignition-temperature of any fixed concentration of mixture cannot be determined by this method, as could also be judged from the obvious permeability of the soap film to some of the vapours used.

The results obtained during this investigation appear to indicate that the soap-bubble method of determining ignition-temperatures as described by McDavid gives values for the ignition-temperature which appear to be erroneous. A radical modification of the method could probably be made, however, which would give more satisfactory results. For instance, a soap-bubble of the mixture under examination might be introduced into a vertical tubular furnace, the bubble being shielded from radiation until at the desired spot. In this case, the results would be far more likely to be correct, as the temperature at which ignition took place would be known, and surface action would be partly eliminated.

Summary.

The soap-bubble method described by McDavid (*loc. cit.*) has been applied to determine the ignition-temperatures of certain mixtures of ether, benzene, light petroleum, and hydrogen with air. The conditions under which consistent results can be obtained are given.

After careful standardisation, the results given by this method were found to be affected by the physical state of the igniting surface and the nature of the material of which it was made; even the addition of small quantities of the salts used for standardisation purposes altered the results obtained. This seemed to show that the method could scarcely give the true ignition-temperature of a gas mixture. The ignition-temperature of a particular gas mixture as determined by two different coils often varied by more than 150° , and results appeared to indicate that the method was not strictly trustworthy even for comparative purposes.

In conclusion, the authors desire to express their thanks to Messrs. Nobel's Explosives Co., Ltd., for whom the work was carried out, and to Mr. Wm. Rintoul, Manager of the Research Section, for permission to publish the results, and to Mr. A. W. Sanderson for his kind assistance in carrying out some of the experimental work.

THE RESEARCH LABORATORIES,
ARDEER FACTORY,
STEVENSTON.

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CXVII.—*The Interaction of Chlorine and Hydrogen. The Influence of Mass.*

By DAVID LEONARD CHAPMAN and JOHN REGINALD HARVEY
WHISTON.

AFTER investigating the precautions which must be taken in order to obtain trustworthy actinometric measurements of the velocity of the photochemical action of chlorine and hydrogen, Chapman and Underhill (T., 1913, **103**, 496) examined the influence of the concentration of hydrogen on this reaction. The determinations were made with mixtures containing small measured quantities of oxygen, and in the same series of determinations the concentrations of chlorine and oxygen in the mixtures were kept constant, whilst the concentration of hydrogen was varied. They found that "as the partial pressure of the hydrogen is increased from zero, the rate of formation of hydrogen chloride per unit volume of the mixture is at first almost proportional to the concentration of the hydrogen, but the ratio of partial pressure of hydrogen to velocity of interaction rises continuously in value as the propor-

tion of hydrogen is increased, and when the pressure of hydrogen has attained a definite value the rate of formation of hydrogen chloride becomes a maximum, and then, as the proportion of hydrogen is still further increased, the rate of interaction of chlorine and hydrogen falls very slowly."

It had previously been shown by Chapman and MacMahon (T., 1909, 95, 959) that the sensitiveness of electrolytic gas at atmospheric pressure is approximately inversely proportional to the concentration of the oxygen it contains for proportions of oxygen varying between 0.08 and 1 per cent. by volume of the electrolytic gas.

These two results were interpreted by a theory advanced by Burgess and Chapman (T., 1906, 89, 1433).

It was our intention to proceed with the investigation of the influence of the concentration of the chlorine on the rate of formation of hydrogen chloride. However, before we were able to complete our investigation, Bodenstein and Dux (*Zeitsch. physikal. Chem.*, 1913, 85, 297) published the result that the reaction is of the second order in the case of a mixture containing equal volumes of chlorine and hydrogen and a small fixed proportion of oxygen. Our results mentioned above on the influence of the concentrations of hydrogen and oxygen were in the main confirmed by these authors.

It will be remembered that Wildermann (*Phil. Trans.*, 1902, 199, 337) also found that the rate of formation of carbonyl chloride when a mixture containing equal volumes of carbon monoxide and chlorine was exposed to light of constant intensity was proportional to the square of the pressure of the interacting gases.

From Bodenstein and Dux's result and the facts that the rate of interaction is inversely proportional to the concentration of the oxygen and nearly independent of the concentration of the hydrogen (provided that this concentration is not too small), it can obviously be deduced that the rate of formation of hydrogen chloride when a fixed volume of electrolytic gas is exposed to homogeneous light of constant intensity is given approximately by the formula

$$\frac{d[\text{HCl}]}{dt} = \frac{k \cdot I \cdot [\text{Cl}_2]^2}{[\text{O}_2]}$$

in which k is a constant and I the intensity of the radiation.

Bodenstein and Dux confirmed the above formula with measurements made with mixtures containing unequal volumes of hydrogen and chlorine.

It may be stated immediately that we are unable to confirm the work of Bodenstein and Dux on the influence of the concen-

tration of the chlorine on the rate of the change. In fact, we find that, within wide limits of concentration of the interacting gases, the rate of formation of hydrogen chloride is given with fairly close approximation by the expression $\frac{k \cdot I \cdot [\text{Cl}_2]}{[\text{O}_2]}$, or, in other words, since $I \cdot [\text{Cl}_2]$ is proportional to the radiation absorbed per second, the hydrogen chloride formed is nearly directly proportional to the radiation absorbed and inversely proportional to the concentration of the oxygen.

The result embodied in the above expression for the rate of formation of hydrogen chloride in mixtures of compositions and pressures within the limits used in our experiments can be easily interpreted by the hypothesis of Chapman, Burgess, Gee, and Underhill. Briefly, the hypothesis in question postulates that the radiation is absorbed by the chlorine molecules. The absorbed energy in the molecules is gradually degraded. In the earlier stages, when the energy is still in a highly efficient form, the degradation is accomplished very rapidly and completely by the agency of oxygen and the other inhibitors. The degradation accomplished in this way is so complete that the resulting degraded energy is no longer capable of assisting the union of the chlorine and hydrogen. The absorbed energy in the chlorine molecules which escapes being degraded in the earlier stages by the inhibitors is transformed to lower forms of energy, which, although capable of activating the chlorine, are to a much less degree, and possibly not at all, degraded by the inhibitors. In other words, the life of an activated molecule is not shortened by the agency of the inhibitors.

Consider unit volume of the mixture of gases exposed to light of intensity I . The rate of accumulation of efficient energy will be $k_1 \cdot I \cdot [\text{Cl}_2]$, k_1 being now and below taken to represent a constant.

The loss of efficient energy is due to two causes, namely, its degradation during the impacts of the chlorine molecules with oxygen molecules and the conversion of the chlorine molecules into the activated form. When, however, the proportion of oxygen to electrolytic gas is as high as 1 per cent. (as it was in all the experiments to be described below), the sensitiveness is almost one hundred times less than that of the purest electrolytic gas we could prepare, and therefore with such a large proportion of oxygen present, the loss of accumulated efficient energy must be almost entirely due to the first of the above-mentioned causes.

Now the number of impacts per second between chlorine molecules and oxygen molecules is given by the expression

$k_3 \cdot [\text{O}_2][\text{Cl}_2]$. Further, if it be assumed that in the mean a constant proportion of the efficient energy is degraded during an impact of a chlorine molecule with an oxygen molecule, the degradation of energy during a single impact will be, in the mean, $k_3 \epsilon$, ϵ being the mean efficient energy of a chlorine molecule after the steady state is reached.

The rate of loss of efficient energy will be the product of the loss during a single impact and the number of impacts per second, which is $k_2 \cdot k_3 \cdot \epsilon \cdot [\text{O}_2][\text{Cl}_2]$.

Equating this to the rate of accumulation of efficient energy, we obtain $k_2 \cdot k_3 \cdot \epsilon \cdot [\text{O}_2][\text{Cl}_2] = k_1 \cdot I \cdot [\text{Cl}_2]$, and therefore

$$\epsilon = \frac{k_1}{k_2 k_3} \cdot \frac{I}{[\text{O}_2]}$$

Now if we make the probable assumption that the rate of formation of active chlorine molecules is proportional to the product of the concentration of the chlorine and mean efficient energy of a single molecule,* the number of active molecules formed per second should be

$$\frac{k_1 \cdot k_4}{k_2 \cdot k_3} \cdot \frac{I \cdot [\text{Cl}_2]}{[\text{O}_2]}$$

but when the pressure of the hydrogen exceeds 15 cm., and possibly at much lower pressures, almost all the active molecules of chlorine combine with hydrogen (Chapman and Underhill, *loc. cit.*), and the rate of formation of hydrogen chloride becomes equal to the active molecules of chlorine produced per second and almost independent of the pressure of the hydrogen.

Therefore the number of molecules of hydrogen chloride formed per second is also given by the expression

$$\frac{k_1 \cdot k_4}{k_2 \cdot k_3} \cdot \frac{I \cdot [\text{Cl}_2]}{[\text{O}_2]}$$

That is, the hydrogen chloride produced is proportional to the radiation absorbed and inversely proportional to the concentration of the oxygen.

If, as we have reason to believe is the case, hydrogen is a weak inhibitor (Chapman and Underhill, *loc. cit.*), the expression for the rate of formation of hydrogen chloride molecules would become

$$\frac{k_1 \cdot k_4}{k_2 \cdot k_3} \cdot \frac{I \cdot [\text{Cl}_2]}{[\text{O}_2] + k_5 [\text{H}_2]}$$

* This assumption is equivalent to the assumption that the tendency of each quantum of efficient energy to change its form is independent of the concentration of the chlorine.

1268 THE INTERACTION OF CHLORINE AND HYDROGEN.

in which k_3 is a constant of small magnitude. Since in our experiments, however, the pressures of the hydrogen and the oxygen have been varied in the same ratio, our results are in equal agreement with both formulæ, and fail to distinguish between them.

EXPERIMENTAL.

Experiments with the Moist Gases.—The apparatus used was a form of Bunsen and Roscoe's actinometer, in which the pressure of the contained gas could be varied, very similar to that used by Chapman and Underhill. The precautions taken in making the measurements and to ensure purity of materials were the same as those observed by Chapman and Underhill.

The mixture of gas experimented with was electrolytic gas which contained about 1.3 per cent. of oxygen by volume. The sensitiveness of the mixture at a pressure of one atmosphere and half an atmosphere was measured, and the results are tabulated below.

Number of experiment.	Sensitiveness at one atmosphere.	Sensitiveness at half an atmosphere.
1.	1000	1029
2.	1000	973
3.	1000	1060

Accordingly, with the moist gases the total hydrogen chloride formed in unit time is almost independent of the pressure, whereas if Bodenstein and Dux's result were correct, the rate of formation of hydrogen chloride ought to be proportional to the pressure.

Experiments with the Dry Gases.—For these experiments, the apparatus was modified in one or two respects. The mixture of gases before use was confined in a gas-holder over sulphuric acid. The sulphuric acid which the holder contained was saturated with chlorine and boiled several times, and the gas-holder was so constructed that the sulphuric acid did not come into contact with the air of the laboratory. The actinometer was the same as that used in the experiments with the moist gases, with the exception that the index contained sulphuric acid and the insolation vessel was horizontal and contained anhydrous copper sulphate spread uniformly over the bottom of the tube to serve as an absorbent of the hydrogen chloride. The copper sulphate was carefully dehydrated in the insolation vessel and heated in a current of chlorine at about 300° for an hour. The internal diameter of the insolation vessel was 2.6 cm. The results are tabulated below

Number of experiment.	Sensitiveness at one atmosphere.	Sensitiveness at half an atmosphere.	Sensitiveness at a quarter of an atmosphere.
1.	1000	963	755*
2.	1000	938	—
3.	1000	944	776*
4.	1000	—	—
5.	1000	—	758*
			752*

* At this low pressure it is possible that many of the activated chlorine molecules lose their activity before making fruitful impacts with the hydrogen molecules (compare Chapman and Underhill, *loc. cit.*).

Bodenstein and Dux admit that inhibitors were gradually produced in the insolation vessel during an experiment, and these inhibitors would tend to increase the apparent order of the reaction. They claim to have eliminated the effect of these inhibitors by the method of conducting their experiments, but it seems to us most likely that the discrepancy between their results and ours is due to this cause.

We take this opportunity of gratefully acknowledging a generous grant awarded to one of us by the Board of Scientific and Industrial Research.

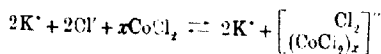
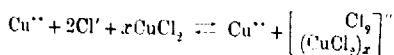
THE SIR LEOLINE JENKINS LABORATORIES,
JESUS COLLEGE,
OXFORD.

[Received, October 13th, 1919.]

CXVIII.—*Auto-complexes in Solutions of Cupric Chloride and Cupric Bromide.*

By STEWART BYRON WATKINS and HENRY GEORGE DENHAM.

In a paper by Donnan and Bassett (T., 1902, **81**, 939), the view is expressed that the changes in colour brought about in solutions of copper and cobalt salts by changes in concentration and temperature, as well as by the addition of certain other haloid salts, are to be attributed to the formation of complex anions, as exemplified in the following equations:



the colour of the anions so formed differing essentially from the colour of the cupric and cobalt ions. Quantitative support to this theory was first afforded by Kohlschütter's migration experiments (*Ber.*, 1904, **37**, 1193), whilst the investigations of one of the authors (*Zeitsch. physikal. Chem.*, 1909, **65**, 64) have shown that in concentrated aqueous and alcoholic solutions of copper and cobalt haloid salts, the cations have a migration number which is distinctly negative. The present paper is an extension of the investigation, and deals with the effect of temperature and concentration on the migration number of the cupric ion.

The experimental method adopted was practically the same as in the former paper, and the results obtained are of the same order of accuracy. Experiments were nearly always carried out in duplicate, and the middle layer was repeatedly analysed.

Below are the experimental results:

TABLE I.

Copper Chloride in Aqueous Solution. Temperature, 35°.

<i>Before electrolysis :</i>	Expt. 1.	2.	3.	4.
Water, grams	13.6121	9.1827	7.931	2.1160
Copper, grams	0.3455	0.4368	1.0695	0.5273
Concentration in gram-mols per litre	0.25	0.75	2.1	4.0
<i>After electrolysis :</i>				
Cathode liquid, grams	36.0216	35.4874	41.2016	46.1836
Copper found in cathode liquid, grams	0.8176	1.4775	4.2870	7.5189
Voltameter Ag	0.2272	0.2718	0.2750	0.1994
Equivalent Cu	0.0669	0.0808	0.0810	0.0587
Copper on cathode	0.0735	0.0832	0.0252	nil.
Cuprous copper in solution ...	0.0604	0.0784	0.1368	0.1173
Cuprous chloride in solution	0.0941	0.1221	0.2126	0.1828
Cupric copper in solution ...	0.8112	1.3991	4.1702	7.4016
Cupric chloride in solution ...	1.7170	2.9605	8.8256	15.6942
Total salt	1.8111	3.0826	9.0382	15.8770
Water	34.2105	32.4048	32.1634	30.3066
Migration number	0.34	0.24	-0.06	-0.57

Temperature, 45°.

<i>Before electrolysis :</i>	Expt. 1.	2.	3.	4.
Water, grams	13.6131	9.1827	6.8970	8.1700
Copper, grams	0.3455	0.4368	0.9180	1.6600
Concentration in gram-mols. per litre	0.25	0.75	2.1	3.2
<i>After electrolysis :</i>				
Cathode liquid, grams	32.0180	41.1732	43.9082	48.4132
Copper found in cathode liquid, grams	0.6848	1.7113	4.5420	6.3680
Voltameter Ag	0.3659	0.3048	0.2611	0.3105
Equivalent Cu	0.1052	0.0898	0.0770	0.0915

TABLE I. (continued).

Copper Chloride in Aqueous Solution. Temperature, 45°.

<i>After electrolysis :</i>	Expt. 1.	2.	3.	4.
Copper on cathode	0.1161	0.0978	0.0322	nil.
Cuprous copper in solution ...	0.0942	0.0820	0.1217	0.1829
Cuprous chloride in solution	0.1467	0.1277	0.1896	0.2849
Cupric copper in solution.....	0.5906	1.6293	4.4203	6.6851
Cupric chloride in solution ...	1.2500	3.4460	9.3520	14.1500
Total salt	1.3967	3.5737	9.5416	14.4349
Water	30.6213	37.5995	34.3066	33.9783
Migration number	0.22	0.135	-0.01	-0.40

TABLE II.

Copper Bromide in Aqueous Solution. Temperature, 35°.

<i>Before electrolysis :</i>	Expt. 1.	2.	3.	4.
Water, grams	21.976	6.8659	2.2323	1.2527
Copper, grams	0.5036	0.3302	0.2246	0.2847
Concentration in gram-mols. per litre	0.36	0.76	1.6	3.6

<i>After electrolysis :</i>	Expt. 1.	2.	3.	4.
Cathode liquid, grams	42.5353	41.5343	48.6760	57.9704
Copper found in cathode liquid, grams	0.8739	1.6396	3.6298	7.3307
Voltameter Ag	0.0893	0.1891	0.1857	0.2000
Equivalent Cu	0.0272	0.0558	0.0547	0.0589
Copper on cathode	0.0394	0.0908	0.0005	nil.
Cuprous copper in solution ...	0.0194	0.0207	0.1089	0.1177
Cuprous bromide in solution	0.0368	0.0467	0.2461	0.2660
Cupric copper in solution.....	0.8590	1.6189	3.5209	7.2130
Cupric bromide in solution ...	3.0200	5.6901	12.3752	25.3589
Total salt	3.0568	5.7368	12.6214	25.6249
Water	39.4785	35.7975	36.0546	32.3455
Migration number	0.32	0.16	0.05	-0.35

Temperature, 45°.

<i>Before electrolysis :</i>	Expt. 1.	2.	3.
Water, grams	10.7732	2.2323	1.2527
Copper, grams	0.2518	0.2246	0.2847
Concentration in gram-mols. per litre	0.35	1.6	3.6

<i>After electrolysis :</i>	Expt. 1.	2.	3.
Cathode liquid, grams	40.8411	49.4290	52.5873
Copper found in cathode liquid, grams	0.7959	3.6765	6.6333
Voltameter Ag	0.2205	0.1673	0.1937
Equivalent Cu	0.0651	0.0489	0.0570
Copper on cathode	0.1068	nil	nil
Cuprous copper in solution	0.0233	0.0977	0.1140
Cuprous bromide in solution	0.0526	0.2206	0.2576
Cupric copper in solution.....	0.7726	3.5788	6.5193
Cupric bromide in solution	2.7169	12.5821	22.9200
Total salt	2.7695	12.8027	23.1776
Water	38.0716	36.6263	29.4061
Migration number	0.19	-0.18	-0.88

TABLE III.

Copper Bromide in Ethyl Alcohol. Temperature, 35°.

<i>Before electrolysis :</i>	Expt. 1.	2.	3.
Alcohol, grams	10.3713	9.0477	5.8932
Copper, grams	0.1441	0.2517	0.5059
Concentration in gram-mols. per litre	0.21	0.43	1.3
<i>After electrolysis :</i>			
Cathode liquid, grams	13.3029	13.7986	16.7181
Copper found in cathode liquid, grams	0.1464	0.3244	1.0655
Voltmeter Ag	0.1124	0.0985	0.1065
Equivalent Cu	0.0332	0.0300	0.0314
Copper on cathode	0.0151	0.0114	0.0176
Cuprous copper in solution	0.0512	0.0466	0.0452
Cuprous bromide in solution	0.1156	0.1052	0.1021
Cupric copper in solution	0.0952	0.2788	1.0203
Cupric bromide in solution	0.3345	0.9767	3.5871
Total salt	0.4501	1.0819	3.6802
Alcohol	12.8528	12.7167	13.0289
Migration number	-0.51	-0.60	-1.1

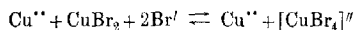
Temperature, 45°.

<i>Before electrolysis :</i>	Expt. 1.	2.	3.
Alcohol, grams	10.3713	9.0477	5.2739
Copper, grams	0.1441	0.2517	0.3822
Concentration in gram-mols. per litre	0.21	0.43	1.17
<i>After electrolysis :</i>			
Cathode liquid, grams	13.5570	14.0426	15.8708
Copper found in cathode liquid, grams	0.1495	0.3282	0.8582
Voltmeter Ag	0.1033	0.0822	0.1229
Equivalent Cu	0.0305	0.0243	0.0362
Copper on cathode	0.0098	0.0103	0.0270
Cuprous copper in solution	0.0510	0.0382	0.0454
Cuprous bromide in solution	0.1152	0.0862	0.1025
Cupric copper in solution	0.0985	0.2900	0.8128
Cupric bromide in solution	0.3463	1.0038	2.8576
Total salt	0.4615	1.0900	2.9601
Alcohol	13.0955	12.9526	12.9107
Migration number	-0.77	-0.90	-1.35

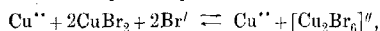
Discussion of Results.

The boundary migration experiments described by Steele (*Zeitsch. physikal. Chem.*, 1902, **40**, 689) and by Donnan and Bassett (*loc. cit.*), supported by the quantitative migration experiments of Kohlschütter (*loc. cit.*) and of Denham (*loc. cit.*), have afforded considerable support to the theory of complex-formation in concentrated solutions of copper and cobalt salts. In Denham's experiments it was found that at 25° the migration number of

copper in a 5.29 solution of copper bromide reached the strikingly low value -0.39 . This was interpreted by assuming that in such solutions complex anions of the type $[\text{CuBr}_4]''$, $[\text{Cu}_2\text{Br}_6]''$, etc., carried copper out of the cathode compartment. Thus, assuming that the equilibrium



lies almost wholly to the right, the migration number would be approximately zero, whilst if appreciable $[\text{Cu}_2\text{Br}_6]''$ ions were present, as demanded by the equilibrium



values less than zero would result.

The parallelism between the migration number and the colour of the solution is shown in table IV.

TABLE IV.

Copper Bromide in Water. Temperature, 25°.

Concentration.	u „	Colour.
0.106	0.445	bluish-green.
0.414	0.440	green.
1.690	0.069	brownish-green.
2.218	0.052	„
3.187	-0.086	brown.
4.055	-0.159	deep brown.
5.288	-0.392	„

On the other hand, many have sought an explanation of this colour-change in the hydration either of the dissolved salt or of the copper cation (notably Biltz, *Zeitsch. physikal. Chem.*, 1902, **40**, 185; Jones and his pupils, *Carnegie Publ.*, No. 60; for complete bibliography, see *Zeitsch. physikal. Chem.*, 1909, **65**, 641). The solution round the cathode may thus become weaker, not only by the wandering away of complex anions containing copper, but by solvent molecules being transported into the cathodic compartment attached to the cation.

That such a transport of solvent molecules attached to ions may occur has been proved by Washburn (*Tech. Quart.*, 1908, **21**, No. 2), although in the cases studied the effect of hydration on migration ratios is not a marked one. Moreover, in their critical review of migration numbers, Noyes and Falk (*J. Amer. Chem. Soc.*, 1911, **33**, 1436) have shown that the true migration number is connected with the apparent or hydrated migration number by the equation

$$T^{Tr} = T + \Delta N_0 \cdot N / N_0$$

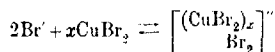
where ΔN_0 is the number of molecules of water transported to the cathode per faraday; N =number of equivalents of salt in solution associated with N_0 molecules of solvent; T =ordinary migration number (referred to solvent, which is assumed stationary); T^{Tr} =true migration number referred to a non-migrating substance.

If one accepts the hydration value obtained by Jones (*Carnegie Publ.*, No. 60, p. 85), this correction in concentrated solutions is of the order of 5–10 per cent., and therefore negligible in the light of the marked negative values obtained.

The effect of such a "hydration" effect will naturally be the more noticeable in concentrated solutions, but Bein's results (*Zeitsch. physikal. Chem.*, 1898, **27**, 50) for calcium chloride—a salt which, according to Abegg and Bodländer's complex theory (*Zeitsch. anorg. Chem.*, 1899, **20**, 453), should not form complex anions, and, according to Jones (*loc. cit.*), has a strongly hydrated cation—show how small this probable hydration effect is.

Chlorine, per cent.	Tempera- ture.	n_{\pm} .
0.039	22°	0.447
0.42	24	0.405
0.99	21	0.390

Donnan and Bassett's theory postulates that the formation of the complex anion in solutions of copper and cobalt salts is attended by the absorption of heat, that is, it is favoured by a rise of temperature. Thus a solution of cobalt chloride in alcohol, which is blue at the ordinary temperature, becomes pinkish-red on cooling to -79° . If this is the case, an increase in temperature should bring about a decrease in the migration number due to the equilibrium



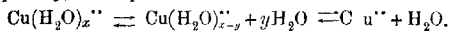
being driven to the right.

On the other hand, the effect of increasing temperature on a hydrated ion will be in all probability to cause a dissociation into a less hydrated or even an anhydrous ion (Lewis, *Zeitsch. physikal. Chem.*, 1905, **52**, 222; 1906, **56**, 223; Biltz, *loc. cit.*; Jones, *loc. cit.*). Jones and West have measured the temperature-coefficients of a large number of salts of varying degree of hydration, and they have concluded that:

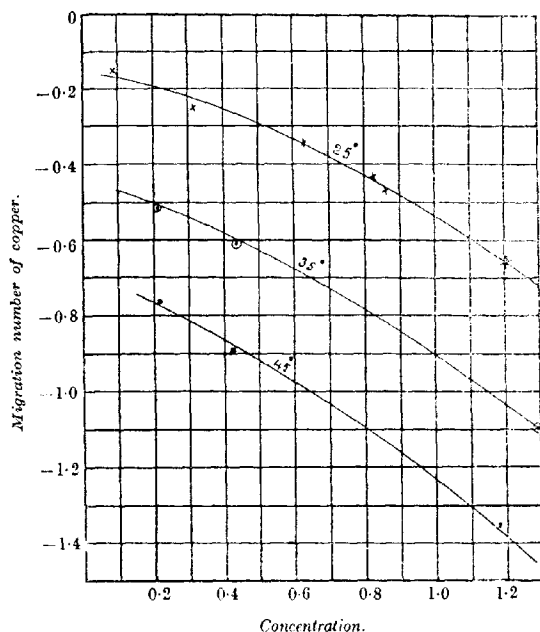
- (1) The temperature-coefficients of aqueous solutions of electrolytes are greater the greater the hydrating power of the electrolyte.

(2) This large increase in conductivity with rise of temperature, in the case of salts forming hydrated ions, is due, in part, to the decreasing complexity of the hydrates formed around the ions.

Consequently, the equilibria



will be driven to the right, and abnormally low migration numbers must consequently tend to approach the normal value (0.4 approx.) with rise of temperature should the abnormality arise from a hydration effect.



In the diagram, the experimental results for copper bromide in alcohol are plotted as a typical example of the definite influence of temperature on the results.

These curves and the tables bring out clearly the rapid decrease in the migration number as the temperature of the solution rises in precise agreement with the demands of the complex theory, in direct contradiction to the demands of Jones' hydration theory.

Moreover, the following results of Bein for salt solutions, wherein

complex formation is scarcely to be expected, bear out the contention that the temperature has very slight influence on the cathodic migration number, even where the evidence of Jones and others indicates that such ions are more or less hydrated.

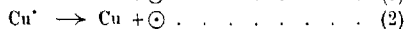
Calcium Chloride.

Chlorine, per cent.	Tempera- ture.	u_{Ca} .
0.42	24°	0.405
0.42	97	0.426
0.77	20	0.395
0.85	94	0.451

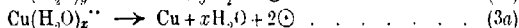
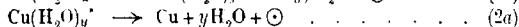
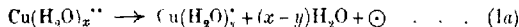
Lithium Chloride.

Chlorine, per cent.	Tempera- ture.	u_{Li} .
0.036	20°	0.371
0.036	97	0.389
0.20	25	0.324
0.20	97	0.381

The most convincing evidence of the presence of auto-complexes in the solutions under discussion is, however, afforded by a consideration of the cathodic copper deposit. In a solution of a copper salt, the mechanism of the electrode process may be represented by any one of the three equations:



or, assuming hydration:



(see Foerster and Seidel, *Zeitsch. anorg. Chem.*, 1897, **14**, 106; Foerster and Coffetti, *Zeitsch. Elektrochem.*, 1904, **10**, 736; Bose, *ibid.*, 1898, **5**, 163; Heiberg, *ibid.*, 1903, **9**, 137; Abel, *ibid.*, 1903, **9**, 268; Bodländer and Storbeck, *Zeitsch. anorg. Chem.*, 1897, **14**, 106; Luther, *Zeitsch. physikal. Chem.*, 1900, **34**, 488; 1901, **36**, 385; Wohlwill, Borchers's "Elektrometallurgie," 3rd Ed., p. 198).

Should equation (3) or (3a) represent the cathode process, the ratio $\frac{\text{weight of copper deposited}}{\text{weight of silver in voltameter}} = 0.295$, whilst any of the other equations would lead to the value 0.590. Table V shows how

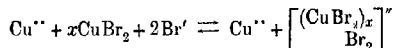
much the experimental values differ from these. In this table, the last column gives the ratio $\frac{\text{weight of copper deposited}}{\text{weight of silver in voltameter}}$.

TABLE V.

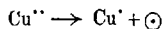
Salt.	Solvent.	Tempera- ture.	Concen- tration.	w_{Cu}	$\frac{Cu}{Ag}$.
$CuBr_2$	water	35°	0.36	0.32	0.44
"	"	35	0.76	0.16	0.48
"	"	35	1.60	0.05	0.002
"	"	35	3.60	-0.35	0.000
"	"	45	0.36	0.19	0.44
"	"	45	1.60	-0.18	0.00
"	"	45	3.60	-0.88	0.000
$CuCl_2$	"	35	0.25	0.34	0.324
"	"	35	0.75	0.24	0.308
"	"	35	2.00	0.181	0.090
"	"	35	4.00	-0.57	0.000
"	"	45	0.25	0.225	0.317
"	"	45	0.75	0.135	0.177
"	"	45	—	0.01	0.123
"	"	45	—	0.4	0.000
$CuBr_2$	alcohol	35	0.21	-0.51	0.134
"	"	35	0.43	-0.60	0.115
"	"	35	1.30	-1.1	0.165
"	"	45	0.21	-0.77	0.095
"	"	45	0.43	-0.90	0.125
"	"	45	1.17	-1.35	0.219

These figures show that in dilute aqueous solutions much of the current is carried by the discharge of cupric to cuprous ions, and, indeed, actual observation showed that the deposits consisted of a heterogeneous mixture of copper and cuprous haloid salt. In such solutions, the electrode processes included in the equations (1) and (3), or, assuming hydration, (1a) and (3a), prevail, the cuprous ion being immediately precipitated as the insoluble chloride or bromide. The extent to which either process occurs has been shown by Seidel and others (*loc. cit.*) to depend on the variables, temperature, concentration, current density, and concentration of acid, and will in no way be influenced by the presence of hydrated ions in solution, whether those solutions are concentrated or dilute. In many of the more concentrated solutions, however, the ratio $\frac{Cu}{Ag}$ shows no quantitative agreement with Faraday's laws, whether the reduction to cuprous ion or to copper itself occurs, or both. In a number of experiments, the ratio $\frac{Cu}{Ag}$ falls to zero, that is, no

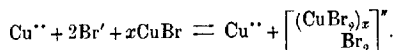
copper or cuprous salt whatsoever is deposited on the cathode. This abnormality, incapable of explanation as it is by the hydration theory, may be satisfactorily explained by the theory of auto-complexes. In concentrated solutions, such equilibria as



are postulated, the undissociated salt, of relatively weak electroaffinity, being forced into a complex anion. As the cuprous ion, however, possesses a more noble potential than does the cupric ion, that is, have a weaker electroaffinity, the cuprous salts, according to Abegg and Bodländer's complex theory (*loc. cit.*), will be more readily forced into a complex than the corresponding cupric salts (Donnan, Abegg's "Handbuch," Kupfer, p. 517). In concentrated solutions, seeing that no metallic copper or copper salt is precipitated on the cathode, the current must be wholly carried in the following way:



(possibly $\text{Cu}(\text{H}_2\text{O})_x^{++} \longrightarrow \text{Cu}(\text{H}_2\text{O})_y' + (x-y)\text{H}_2\text{O} + \ominus$); the cuprous salt, however, instead of being thrown out of solution, as happens in the more dilute solution, and as demanded by the hydration theory, forms a soluble cupri-cupro-salt with the cupric salt already in solution. It is precisely in those solutions where the absence of deposit on the cathode occurs, that the migration number is so strongly negative. The soluble nature of this cupri-cupro-salt, coupled with the markedly negative migration number, points very strongly to the assumption that such a reaction as the following occurs:



In further confirmation of the views here put forward, a migration experiment was carried out in a U tube, first with 4*N*-cupric chloride, and secondly with 4*N*-cupric chloride which had been warmed with cuprous chloride, these lower layers being covered by *N*/10-cupric chloride. In both cases, the brown boundary moved towards the anode.

Summary.

(1) The effect of temperature and concentration on the migration number of solutions (aqueous and alcoholic) of copper bromide and chloride has been investigated.

(2) The effect of increasing temperature and concentration is to cause a marked drop in the migration number of the copper ion, which in concentrated solutions approaches -1 in value.

(3) The formation in concentrated solutions of soluble cupri-ampro-haloid salts at the electrode of the migration vessel has been proved.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF QUEENSLAND,
BRISBANE.

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CXIX.—*Colloidal Electrolytes: Soap Solutions as a Type.*

By JAMES WILLIAM MCBAIN, MARY EVELYN LAING, and
ALAN FRANCIS TITLEY.

BASED on the extensive data obtained from the study of soap solutions in this laboratory since 1908, McBain and Salmon have defined a new class of compounds, colloidal electrolytes, to which a very large number of substances of great industrial importance may be expected to belong. This comprehensive group is defined as comprising salts in which one ion has been replaced by an ionic micelle of high valency, mobility, conductivity, and degree of solvation. Regarded from another point of view, this means that any colloid which carries electrical charges will in some measure approach the behaviour of a typical colloidal electrolyte. Light is also shed on the properties of colloidal solutions which contain acids, bases, or salts, or to which these have been added. The consistent application of this point of view leads to an ionic micelle theory of all charged colloids; the current assumption that the other charge is carried by the solvent is replaced by the hypothesis that free ions of charge equal and opposite to that of the charged colloid are present in the sol or gel.

Soap was chosen as the subject for investigation, not only because of its industrial importance, but because of its known and definite chemical simplicity and constitution as compared with dyes or protein derivatives, etc. Furthermore, chemical literature contained apparently irreconcilable data obtained by a number of well-known authorities, such as Kraft, Smits, and Kahlenberg. These either assumed that soap was an ordinary neutral colloid, or else, on the contrary, an electrolyte which had suffered extreme hydrolysis with the formation of colloidal residue suspended in a strongly alkaline solution. Each investigator, moreover, considered that the whole problem was solved.

Now it is demonstrated through the measurements of con-

ductivity, osmotic activity, and alkalinity of soap solutions communicated from this laboratory that in concentrated solution the soaps are typical colloidal electrolytes. On dilution, they gradually break down into simple salts. In extreme dilution, acid soaps separate out through hydrolysis. Both catalytic and electromotive force measurements have shown that, except in extreme dilution, hydrolysis is a very minor consideration, the hydroxyl ion being present to the extent of only about $N/1000$.

The argument for the existence of the ionic micelle was as follows: In all concentrations the conductivity is high and the osmotic activity, which was measured by the unexceptionable method of dew-point lowering, is only moderate. Hence, in concentrated soap solutions, even if all the osmotic activity is earmarked for the potassium, sodium, or ammonium ion, nearly or quite half of the conductivity remains to be accounted for. This conductivity must evidently be ascribed to some constituent that does not exert appreciable osmotic pressure and that therefore must be colloidal. One of us (J.W.M., *Trans. Faraday Soc.*, 1913, **9**, 99; *Kolloid Zeitsch.*, 1913, **12**, 256) has shown how this is possible and probable by applying the principle of Stokes's law to the hypothesis of a heavily charged, heavily hydrated ionic micelle which would exhibit excellent conductivity and high viscosity at the same time.

Although our investigation of soap solutions has only reached its first stage, it has been possible on the basis of the above reasoning to set up a comprehensive theory which explains and reconciles all the mass of data of the most diverse sort which has already been accumulated. The various details of this theory, beyond the rough outline given above, will be mentioned and discussed in turn as we come to the new and confirmatory experimental evidence described below.

This communication presents measurements of the freezing point and conductivity of nearly all the soap solutions which can be studied at 0° . Such comprise solutions of the potassium salts of the saturated fatty acids up to and including the laurate (C_{12}) in all concentrations, and of the sodium salts up to the octoate (C_8). Further, the values for potassium oleate can be measured up to $0.6N$ ($0.8N$ is a solid jelly at the ordinary temperature), and sodium oleate up to $0.4N$, a solution which is already quite viscous.* All other sodium, potassium, and ammonium soaps

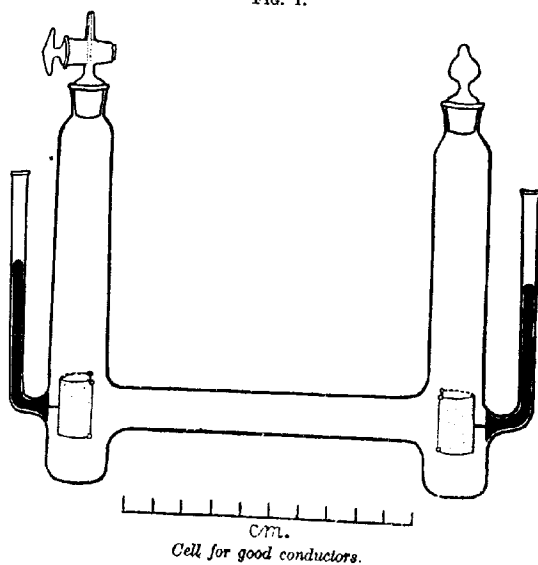
* The stable form of the sodium oleate solutions at 18° is a white curd. The conductivity at 18° of a very slightly alkaline $0.4N$ sodium oleate solution which has solidified to a stiff white curd is still 95 per cent. as great as when it is a clear oily liquid at the same temperature.—M. E. L.

gelatinise, crystallise, sediment, or solidify at temperatures between 10° and 90° , as the case may be. Even potassium laurate and decanoate usually separate out at above 0° . This is another reason why our chief experimental work hitherto has had to be carried out at 90° , in spite of the greatly increased difficulties entailed.

*The Conductivity of Soap Solutions at 18° .**

In all our experiments, the precautions described in previous communications were observed. All instruments and vessels were

FIG. 1.



standardised. The soaps were likewise prepared from potassium drippings and fatty acids by methods previously described. Concentrations are expressed in weight normality, N_w (mols. per 1000 grams of water), and in volume normality, N_v , the latter referring only to the temperature of the particular experiment.

The conductivity measurements of solutions from $N/10$ upwards were carried out in a simple and convenient cell of Jena glass of the form shown in Fig. 1, specially designed for excellent conductors. The large platinum electrodes were coated with grey

* Experiments by M. E. L.

platinum sponge, and they were held firmly in position by glass rods fused to the cell wall and to each corner of the platinum. The cell constant was 13.20. The conductivity water possessed a specific conductivity of $1-2 \times 10^{-6}$, for which no correction was made. Solutions from $N/10$ downwards were studied in the borosilicate cell described by one of us (M.E.L., T., 1918, **113**, 245). The two cells gave identical values for the $N/10$ -solutions.

The results are recorded in tables I—IV. The first column gives the weight normality, N_w , of the soap; the second, the volume normality at 18°, N_v ; the third, the values obtained for the specific conductivity, κ , the values given being the final results from wholly independent solutions; * the fourth,† the density, D_4^{18} ; the fifth, the equivalent conductivity, Λ ; the last column, the apparent degree of dissociation, α , where $\alpha = \mu_v/\mu_\infty$, μ_∞ being taken as equal to 85.4 for potassium salts, except the *n*-octoate (88.2) and sodium oleate (64.3).

TABLE I.

Conductivity of Potassium Laurate at 18.00°.

N_w	N_v	κ	Λ	α
2.000	1.378	0.05947	43.14	0.505
1.500	1.118	0.05131	45.80	0.536
1.000	0.820	$\begin{Bmatrix} 0.03824 \\ 0.03889 \\ 0.03866 \end{Bmatrix}$	47.09	0.551
0.750	0.641	0.03032	47.21	0.553
0.500	0.449	0.02042	45.44	0.532
0.400	0.367	0.01622	44.22	0.518
0.200	0.191	$\begin{Bmatrix} 0.007984 \\ 0.007984 \end{Bmatrix}$	41.77	0.489
0.100	0.098	$\begin{Bmatrix} 0.004322 \\ 0.004299 \end{Bmatrix}$	44.03	0.516
0.050	0.049	0.002713	54.89	0.643
0.0247	0.024	0.001702	68.74	0.805
0.010	0.010	0.0007539	75.44	0.883

TABLE II.

Conductivity of Potassium Oleate at 18.00°.

N_w	N_v	κ	D_4^{18}	Λ	α
0.600	0.540	$\begin{Bmatrix} 0.02023 \\ 0.02013 \end{Bmatrix}$	1.0070	37.25	0.436
0.400	0.363	0.01304	1.0030	36.72	0.430
0.200	0.188	0.006248	0.9999	33.30	0.390
0.100	0.097	0.002877	0.9996	29.74	0.348
0.050	0.049	0.001451	0.9991	29.57	0.346
$N/32$	0.031	0.001035	0.9989	33.32	0.390
0.010	0.008	0.0004198	0.9987	51.95	0.608

* One preparation of oleic acid gave quite colourless clear soap solutions, the other pale yellow solutions.

† Omitted in Tables I and IV, as new determinations were not required.

TABLE III.

Conductivity of Sodium Oleate at 18.00°.

N_w	N_s	κ	D_4^{25}	Λ	α
0.600	0.510	0.01104	1.0050	21.67	0.337
0.400	0.357	{ 0.007362 } { 0.007476 }	1.0020	20.80	0.323
0.200	0.197	{ 0.003994 } { 0.003855 }	0.9997	19.77	0.307
0.100	0.099	0.001922	0.9993	20.46	0.318
0.050	0.049	0.0009966	0.9987	20.59	0.320
0.010	0.010	0.0002956	0.9986	30.09	0.468

TABLE IV.

Conductivity of Potassium n-Octoate at 18.00°.

N_w	N_s	κ	Λ	α
2.000	1.601	0.06757	42.24	0.479
1.000	0.895	0.04208	48.60	0.551
0.750	0.690	0.03345	49.75	0.564
0.500	0.472	0.02455	53.00	0.601
0.200	0.198	0.01185	63.05	0.715
0.100	0.099	0.006456	69.50	0.788

The density in every case is very slightly greater than that of water, as is always observed for potassium and sodium salts of the lower fatty acids.

Some of these solutions have been measured at neighbouring temperatures by other investigators with fewer experimental precautions (Kahlenberg and Schreiner, *Zeitsch. physikal. Chem.*, 1898, **27**, 552; Dennhardt, *Diss.*, 1898; *Ann. Phys. Chem.*, 1899, [iii], **67**, 325; Kurtzmann, *Diss.*, 1914; *Koll. Chem. Beihefte*, 1914, **5**, 465; Reychler, Eighth International Congress of Applied Chemistry). Their results differ more or less irregularly from ours by amounts varying from 0 to 30 per cent. in both directions. The smaller differences are chiefly attributable to alkali dissolved from the glass, an important source of error in the study of soap solutions (see McBain and Taylor, *loc. cit.*, on whose exact study the validity of these experiments is based). On the whole, the agreement is substantial, and our results are probably accurate to about 1 per cent., with the possible exception of sodium oleate.

The effect of time is of the order of magnitude of 1 per cent., but all our solutions were kept for several days at the ordinary temperature to allow them to become quite constant before being measured. The data refer to clear solutions in every case, except *N*/20-potassium laurate, which is always cloudy. Thus many of these solutions are supersaturated or metastable with respect to

the separation of indefinite acid soaps. The latter dissolve on warming, and the metastable solutions can then be preserved for long periods.

The Explanation of the Good Conductivity of these Colloidal Electrolytes, together with their Anomalous Maxima and Minima, by Means of the Hypothesis of the Ionic Micelle.

It will be recollected that hydrolysis has been shown to occur to only a slight extent in concentrated solutions of soap, so that in any case it cannot be adduced to explain an appreciable part of the good conductivity exhibited by soaps (and by hexadecanesulphonic acid and its salts). This must find another explanation.

The conductivity results are best discussed by showing them in the form of a graph for comparison. This is done in Fig. 2, where the equivalent conductivities are plotted as ordinates against the concentration, N_v , as abscissæ. The figure also includes curves for the results of the higher potassium soaps at 90°.

The most striking point about these curves is that they represent moderately good conductivities even in concentrated solutions. Indeed, in many cases the conductivity curve, after passing through a minimum, rises on further concentration to a maximum, a phenomenon otherwise unknown in any aqueous solution,* except for Reychler's hexadecanesulphonic acid, which is also a soap (*Bull. Soc. chim. Belg.*, 1913, **27**, 113). This effect is more pronounced at 18° than at 90°. Again, for any one saturated fatty acid, the potassium salt exhibits this behaviour to a distinctly greater degree than does the corresponding sodium soap. The oleates differ entirely from the soaps of the saturated fatty acids in that sodium oleate is a very much more typical soap in this respect.

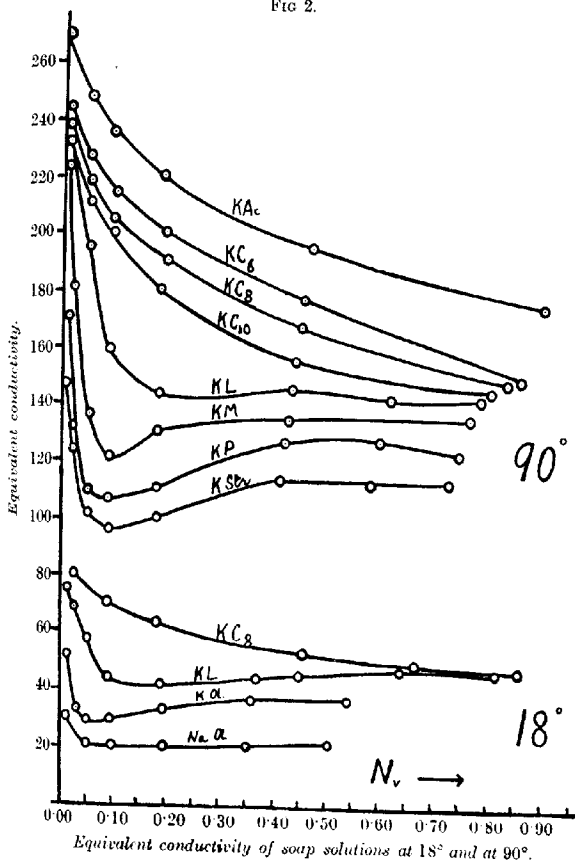
The existence of the minimum as an experimental fact has shown that on further increase of concentration the changes effected are such as to increase the conductivity. This cannot possibly be due to dissociation suddenly increasing again for a limited interval, nor can it be due to free hydroxyl ions, since the latter factor is negligibly small.

The increase of conductivity with increase of concentration must therefore be due to the replacement of the simple laurate anion by an ionic micelle of higher mobility. Thus the effect of decreasing dissociation is more than counterbalanced by this replacement. Finally, however, a maximum is reached where the steadily

* Sloan (*J. Amer. Chem. Soc.*, 1910, **32**, 946) finds that at 0° the equivalent conductivity of aqueous potassium iodide is constant over a considerable range of concentration.

diminishing dissociation of the colloidal electrolyte itself overbalances all other factors. That the conductivity of the ionic micelle is greatest in concentrated solutions, where its hydration is least, will be discussed below.

FIG. 2.



The position of the minimum at the ordinary temperature is still only at $N/5$, but the greater formation of ionic micelle is evinced by the quite slow rise of the curve on dilution at the solution $N/10$ as contrasted with its rapid rise at 90°. This behaviour was predicted by McBain and Salmon, as was also the fact that

the minimum for potassium oleate occurs between $N/10$ and $N/20$ owing to the greater tendency of this higher soap to form micelle.

The Temperature-coefficient of Conductivity of Solutions.

The behaviour just described is in accordance with the abnormally high temperature-coefficient of conductivity in soap solutions, a property which was formerly ascribed to rapid increase of hydrolysis on heating, but is now seen to be the result of diminishing hydration of the ionic micelle with rise of temperature.

The influence of concentration on the temperature-coefficient of the conductivity may be analysed by the use of table V, which gives the ratios between the values at 90° and at 18° , together with those of a few electrolytes for comparison. Kurzmann (*loc. cit.*) has already pointed out that for a $0.6N$ -potassium oleate solution the conductivity rises three-fold between 20° and 90° , whilst the viscosity falls four hundred-fold.

TABLE V.

Ratios between Conductivities at 90° and 18° .

Salt.	$0.01N_{90}$	$0.05N_{90}$	$0.1N_{90}$	$0.2N_{90}$	$0.5-0.6N_{90}$	$1.0N_{90}$	$2.0N_{90}$
Sodium acetate ...	3.25	3.22	3.19	3.13	3.12	3.14	3.33
Potassium acetate	2.88	2.85	2.82	2.79	2.75	2.79	2.98
Sodium hydroxide	2.53	2.46	2.46	2.44	2.45	2.50	—
Potassium hydroxide	—	—	—	—	—	2.22	—
Potassium octoate.	—	—	2.95	3.03	3.18	3.06	—
„ laurate	3.09	3.56	3.62	3.45	3.22	3.04	2.86

It is evident from table V that for electrolytes the ratio between the conductivities at 90° and 20° do not vary much with change of concentration, although they make a flat curve with a minimum at about half normal. Further, the values for sodium salts are in every case 0.3 unit, or about 10 per cent. higher than for the potassium salts. Soaps, on the other hand, possess higher values than the corresponding potassium electrolytes, and they exhibit an opposite behaviour in that the ratio for the temperature effect is a maximum in medium concentration. Kurzmann's ratios, as far as they go, appear to parallel ours, but are 0.3 to 0.4 unit lower.

The customary temperature-coefficients of conductivity involve three separate factors for any electrolyte and five for a colloidal electrolyte. The first two are the specific mobilities of the two ions, of which those with lowest mobility have the highest temperature-coefficient, the third is the change of dissociation with temperature, whilst in the case of a colloidal electrolyte there is

the further factor of the change in equilibrium between ions and ionic micelle in addition to the temperature-coefficient of the latter itself. The more exact analysis is simple for electrolytes, but must remain in abeyance for the soaps until we have obtained the further experimental data contemplated. The higher temperature-coefficient for sodium ion is in accordance with the recognised probability of its hydration being greater than that of potassium, and that the same factor of hydration would explain the data for soap solutions. The increase of colloid with lowering of temperature is also a factor which might conceivably operate in either direction according as to whether this is increase of highly mobile ionic micelle or increase of neutral colloid at the expense of electrolyte and micelle.

The other case of a colloidal electrolyte exhibiting an anomalous conductivity curve is hexadecylsulphonic acid (Reychler, *loc. cit.*), which exhibits a minimum conductivity of 135 mhos. (to 149 mhos.) in *N*/30-solution at 56° (or 55°), but it has been measured only up to *N*/15-solution. Indeed, it is tantalising in the extreme to note how many promising cases of colloidal electrolytes have been studied only in dilute solution, probably the reason why this type of behaviour has not been long familiar.

The Osmotic and Freezing-point Methods.

These data are not nearly so accessible as one might expect for the case of colloidal electrolytes in which we are interested, as a brief examination will show. Indeed, the data of McBain and Salmon constitute the only satisfactory determinations hitherto recorded.

The freezing-point method, which is the subject of our present study, is the osmotic method *par excellence* where it can be applied, but it is here surprisingly limited in its range of application. Its trustworthiness is undisputed, and, further, it may be made accurate. The boiling-point method is wholly untrustworthy in its application to solutions that froth and contain colloids on account of the effects of enclosed air, which, as McBain and Taylor proved experimentally, entirely vitiate the indications of the method, and may lead to large apparent lowering instead of rise of boiling point. The vapour-pressure method, even in the hands of Smits, led to equally erroneous results on account of the same unsuspected error. McBain and Taylor found that weeks of effort were required to obtain a single rather inexact measurement. Osmometer data, again, depend so much on the mode of interpretation that it is inadvisable to build upon such a foundation.

The lowering of dew-point method has been developed by McBain and Salmon, and measurements have been made of nearly a hundred soap solutions. It possessed the double advantage that it could be used at various temperatures, and that the presence of air had no influence on the results. It is, however, an unfamiliar method which has not been previously applied to the study of solutions.

The existing literature consists of two measurements by Kahlenberg and Schreiner of the lowering of freezing point of $N/8$ - and $N/16$ -sodium oleate, and the dew-point data of McBain and Salmon, mostly referring to a temperature of 90° . The freezing-point measurements here presented were carried out in order to study the effect of temperature and obtain further corroborative evidence by this independent method.

The great difficulty is to measure the soaps while in the form of homogeneous solution. On cooling in the freezing apparatus, they usually become turbid, with the formation of fine, white or colourless, crystalline flakes, presumably of somewhat acid soap. This may often be avoided, and the soaps can be measured in the metastable condition. It should be noted that they are only a few degrees below the temperature at which the homogeneous form of the system constitutes stable reversible equilibrium. Indeed, perhaps the most important fact for the whole study of soap solutions is that the solutions constitute perfect reversible equilibria in which colloid, micelle, and crystalloid alike participate (see McBain and Taylor, *loc. cit.*). Incidentally, this would lead us to infer that colloidal systems in general represent the equilibria much more often than is usually recognised, owing to the conditions not being kept constant.

Two methods were used, namely, the ordinary one of Beckmann and that of Richards (*Zeitsch. physikal. Chem.*, 1903, **44**, 563; *J. Amer. Chem. Soc.*, 1903, **25**, 291). The latter is the quickest, and probably also the most accurate, of the precision methods, and it had been shown to be capable of yielding results accurate to about 0.0003° . It consists of the use of a Dewar vacuum vessel surrounded by a bath of the freezing temperature, and containing a solution which is full of finely powdered pure ice. When, after stirring, equilibria is attained, a portion of the solution is withdrawn for analysis. For the latter we used either a Zeiss interferometer in conjunction with a graph prepared from standard solutions, or else we evaporated the solutions to dryness and weighed the residue. The former method, for example, is suitable for potassium acetate, the latter for potassium laurate. Although our object was not great accuracy, but chiefly trustworthiness and

results free from distortion, we used a standard thermometer graduated in five-hundredths of a degree, the scale and readings of which were corrected to the readings on the international hydrogen thermometer at the Reichsanstalt in 1913, and this thermometer was kept permanently at 0°.

Results by the ordinary Beckmann method are usually much distorted by the effect of the low convergence temperature, which makes the lowering too great. In concentrated solutions, moreover, the alteration of concentration due to undercooling is very appreciable, and tends in the same direction. This error cannot readily be allowed for by the ordinary method of calculation in the case of soap solutions, although it is very marked, probably on account of the protective action of the colloid on incipient ice crystals. Thus, unless an inoculating rod was used, the undercooling easily exceeded 7° for an hour at a time, in spite of vigorous stirring. Great care was taken to minimise undercooling and to raise the convergence temperature. The important point to remember in what followed is that the lowering observed is never less than the true value, but that, on the contrary, the osmotic effect is exaggerated.

The Freezing-point Data.

Table VI presents the results of the Beckmann freezing method. The results marked with an asterisk denote turbid solutions. The potassium myristate (C_{14}) separated out completely on cooling with marked evolution of heat; the liquid froze a few thousandths of a degree below 0°.

TABLE VI.*

Lowering of Freezing Point by Beckmann Method.

	0.2N _w	0.5N _w	1.0N _w	2.0N _w
Potassium acetate.....	0.749°	1.948°	3.82°	8.56°
Sodium acetate	0.704	1.774	3.739	8.10
Potassium <i>n</i> -octoate...	0.742	1.860	2.519	3.146
„ decaate...	0.649	0.752	1.014	—
„ laurate ...	0.197	0.332	0.623	0.355
	0.245	0.371	0.737	1.460

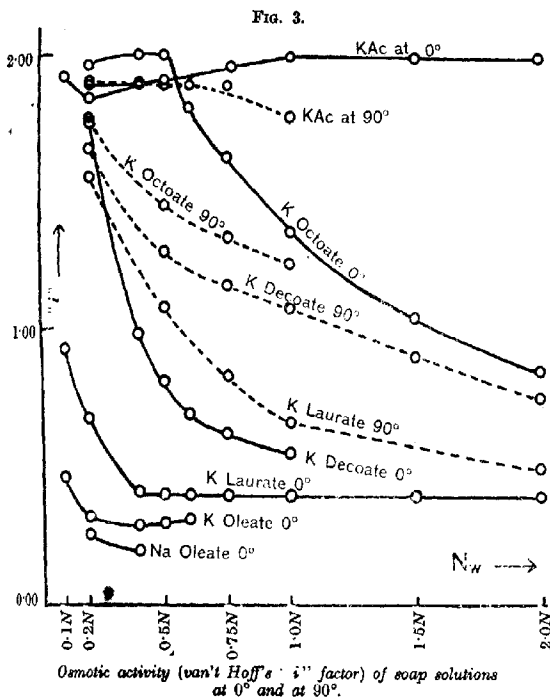
Also 0.75 sodium acetate, 2.740°; 1.5 sodium acetate, 5.83°; 0.05 potassium laurate, 0.177°; 0.1 potassium laurate, 0.212°; 1.0 sodium *n*-octoate, 2.445°; 0.6 potassium oleate, 0.348°; 0.4 potassium oleate, 0.215°; 0.4 sodium oleate, 0.146°; 0.2 sodium oleate, 0.095°; 3.0 potassium *n*-octoate, 4.71°.

* Experiments by M. E. L. or J. W. M.

Table VII contains the results of the Richards method, in which it is a matter of great difficulty to avoid separation of soap with resulting turbidity. Here again such solutions are designated by
..... Successful attempts were made to measure

Also sodium octoate, $1.0N_w$, 1.32; potassium octoate, $3.0N_w$, 2.53.

The lowering of freezing point is so large as to be indisputable, although it is in many of the solutions less than for an electrolyte of the same concentration.



The Effect of Temperature on the Osmotic Activity of Soaps.

The significance of these results is more apparent from a study of the results plotted graphically, as in Fig. 3, in the form of the value of the van't Hoff factor "i." This is merely the ratio between the actual lowering and that predicted theoretically for a perfect non-electrolyte of the same concentration, namely, 1.858° per equivalent of normality. In Fig. 3 the values of "i" are plotted against total weight normality of the solution. Some of the values at 90° are included for comparison.

First, with regard to the absolute magnitude of the osmotic effect in concentration of the higher soaps above $N/3$, it lies between $1/5$ and $2/5$ of that for a crystalloid such as sucrose, or between $1/10$ and $2/10$ of that for an acetate. Further, the osmotic effect tends to be constant for concentrated solutions. At 90° , on the other hand, the osmotic effect is several times greater, and it decreases rapidly with concentration up to $1.5N$ or beyond. Both facts indicate a much more complete formation of colloid at the lower temperature.

Secondly, the familiar general influence of hydration in magnifying osmotic effects is clearly apparent in the data for the acetates, which in turn stimulate complete dissociation in concentrated solution. The effect of hydration is much more in evidence at 0° than at 90° .

The octoate is particularly interesting in its intermediate position in the homologous series as in its behaviour. In solutions up to $N/2$, it is quite like the acetate, although with even greater apparent hydration. From $N/2$ upwards, however, it rapidly and steadily falls, like the decoate at 90° , until the osmotic activity is only 0.85 that of a theoretical (non-hydrated) non-electrolyte.

The Concentration of Potassium or Sodium, and the Mobility of the Ionic Micelle at 18° .

In tables I to IV, values were given for the degree of dissociation deduced from conductivity based on the mobilities $K' = 64.7$, $Na' = 43.6$, $C_3' = 34.7$, $C_8' = 23.5$, $C_{12}' = 20.7$, $C_{18}' = 20.7$, where the fatty acid ions are indicated by the number of carbon atoms they contain. Our data, supplemented by those of Kohlrausch for the acetates, when calculated lead to the provisional concentration of alkali ions given in table IXa. This tacitly assumes that even the ionic micelle exhibits the same conductivity as the ions from which it originates. An alternative basis of calculation is contained in table IXb, to be explained below.

TABLE IX.

Concentration of Potassium or Sodium at 18° .

(a) *Assuming Ordinary Ionic Mobilities.*

Substance.	0.1N.	0.2N.	0.4N.	0.5N.	0.6N.	1.0N.	2.0N.
Potassium acetate.....	0.084	0.159	0.298	0.360	0.422	0.634	1.002
Sodium acetate	0.069	0.129	0.235	0.278	0.324	0.467	0.680
Potassium octoate ...	0.079	0.143	0.261	0.300	0.350	0.551	0.958
„ laurate ...	0.052	0.098	0.207	0.265	0.324	0.551	1.01
„ oleate	0.035	0.078	0.172	0.217	0.262	—	—
Sodium oleate	0.032	0.061	0.129	0.165	0.192	—	—

TABLE IX. (continued).

(b) If Ionic Micelle has the same Mobility as Potassium.

Substance.	0.1N.	0.2N.	0.4N.	0.5N.	0.6N.	1.0N.	2.0N.
Potassium octoate ...	0.079	0.143	0.251	0.300	0.342	0.504	0.822
" laurate ...	0.034	0.065	0.137	0.176	0.214	0.36	0.65
" oleate	0.023	0.051	0.114	0.143	0.173	—	—
Sodium oleate	0.019	0.037	0.077	0.098	0.120	—	—

Taking, first, the tentative results of table IXa for the oleates and laurate, and comparing them with the data of table VIII, it is at once apparent that the supposed concentration of potassium or sodium greatly exceeds the total concentration of colloidal matter present, except for the most dilute solutions. Thus, for 0.4N-solutions, the discrepancies amount to about 0.05N.

We are forced to revise the assumption made with regard to the conductivity of the ionic micelle, and to ascribe to it a conductivity equal to that of the potassium if conductivity and osmotic measurements are to be harmonised at all. In table IXb, then, the conductivity data are calculated on the assumption that the ionic micelle has an equivalent conductivity of 64.7, which is more than three times as great as that of the true oleate or oleate ion. This is, however, in agreement with the theoretical considerations advanced by one of us (J.W.M., *Trans. Faraday Soc.*, 1913, **9**, 99; *Kolloid Zeitsch.*, 1913, **13**, 56), and already applied by one of us in a previous communication with Salmon (*loc. cit.*). It was found necessary to make a similar assumption in the case of concentrated solutions at 90°.

Once again it is necessary to recall that the known sources of distortion of the experimental data operate in such direction as to emphasise the argument on which our conclusions are based. Thus, owing presumably to hydration, osmotic data in general are obviously magnified (see, for example, Landolt-Börnstein "Tabellen," where apparent dissociation frequently exceeds 100 per cent.). Again, high viscosity is conceded to have the effect of diminishing apparent conductivity. Yet, in spite of this, the outstanding experimental result is that in soap solutions the osmotic effect is only sufficient to explain about half of the conductivity exhibited.

The effects just discussed for the case of ordinary electrolytes are exemplified in the usual unmistakable fashion by the results for the acetates and the more dilute solutions of the octoate. In these cases, the osmotic activity as measured considerably exceeds the total predicted from conductivity. In the more concentrated solutions of octoate, however, the soap character predominates

sufficiently to mask this, and they show more than 50 per cent. of colloid (see below, table X).

In this intermediate case of potassium octoate in table IX, use was made of Fig. 3 in computing the average mobilities of the varying mixtures of ions and ionic micelle here present. For solutions between 0.5 and 2.0*N*, it was simply assumed that A_{∞} varied linearly with the i value from 88.2 for $i=2.00$ to 108.3 for $i=0.40$. This is a first approximation pending the results of actual measurements of migration now being carried out with soap solutions.

The Amounts of Crystalloid and Colloid in Soap Solutions.

The total amounts of crystalloidal matter other than potassium or sodion are obtained by subtracting the numbers in table IX for sodium or potassium from those of table VIII for total crystalloids; the results are given in table X. Further, these amounts subtracted from the total concentration leave the amounts which it is necessary to regard as colloid. Further, since the total amount of, say, oleate present must be the sum of crystalloidal and colloidal oleate, the amount of colloid is simply the total concentration less the value for crystalloid given in table X. These values are collected in table XI, and the latter includes for comparison a few results found by the dew-point method at 90°.

TABLE X.

Crystalloidal Matter other than Potassium or Sodium.

Substance.	0.1 <i>N</i> .	0.2 <i>N</i> .	0.4 <i>N</i> .	0.5 <i>N</i> .	0.6 <i>N</i> .	1.0 <i>N</i> .	2.0 <i>N</i> .
Potassium acetate.....	0.106	0.211	0.462	0.580	0.708	1.396	3.598
Sodium acetate	—	0.251	0.525	0.672	0.836	1.543	3.680
Potassium octoate ...	—	0.248	0.559	0.700	0.790	0.856	0.868
" laurate ...	0.059	0.071	0.027	0.02	0.03	0.04	0.13
" oleate	0.023	0.013	0.002	0.007	0.014	—	—
Sodium oleate	—	0.014	0.002	—	—	—	—

TABLE XI.

Total Concentration of Colloid.

Substance.	0.1 <i>N</i> .	0.2 <i>N</i> .	0.4 <i>N</i> .	0.5 <i>N</i> .	0.6 <i>N</i> .	1.0 <i>N</i> .	2.0 <i>N</i> .
Potassium octoate	—	-0.05	-0.06	-0.2	-0.19	+0.144	+1.132
Do. at 90°	—	-0.02	—	+0.07	—	+0.28	—
Potassium laurate	0.041	0.129	0.373	0.48	0.57	0.96	1.87
Do. at 90°	—	-0.01	—	+0.22	—	+0.85	+1.89
Potassium oleate...	0.077	0.187	0.398	0.493	0.586	—	—
Sodium oleate	—	0.186	0.398	—	—	—	—

The results given in tables X and XI may be summarised in the statement that in all but the most dilute solutions of the laurate, and still more so with the oleates, the soap exists almost entirely as colloid. The 0.1*N*- and 0.2*N*-laurate, and the 2.0*N*-octoate, contain comparable amounts each of crystalloid and colloid.

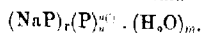
It is instructive to note that the effects of hydration are much less evident at 90°, which agrees well with the extensive investigations of H. C. Jones and others on the solvate theory. The results with soap solutions in general afford strong support for a solvate form of the dissociation theory. For instance, the change in hydration with temperature explains the very high temperature-coefficient of the conductivity of soap solution.

The second effect of temperature is that much more colloid is formed at lower temperatures. This is very evident in the case of the higher soaps. At 90°, as at the ordinary temperature, very dilute solutions of soap contain but little colloid, and the soap is essentially in the form of a simple electrolyte. At the lower temperature, however, the formation of colloid sets in at much lower concentration.

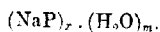
The combined influences just referred to are most apparent in the intermediate case of the octoate. Whereas at the ordinary temperature apparently negative concentrations are deduced for colloid owing to the influence of hydration, even up to 0.6*N*-solution, at 90° the negative value at 0.2*N* is almost within the experimental error, and the formation of colloid shown already at 0.5*N*-solution to the extent of 11 per cent.

The Formulation and Concentration of the Ionic Micelle.

As was shown in the previous communication, the conception of the ionic micelle that appears most probable pending the results of further experiments is that it consists essentially of an aggregation of ordinary ions retaining their original charges. Around this nucleus would be condensed a large number of molecules of water, and probably also most of the neutral colloidal soap available. This is represented in the formula



With increasing concentration, or when the dissociation is diminished, this must tend to alter towards neutral colloid



There was evidence for the conclusion that hydration diminishes and mobility increases with increasing concentration.

We have shown how the approximate values of the concentra-

tions of the total crystalloid and total colloid can be obtained. We have now to allocate the total crystalloid between undissociated soap, sodion or potassion, and simple fatty ion, and the total colloid between neutral colloid, $(\text{NaP})_x$, and aggregated ions in the micelle, $(\text{P})_n^{(1)}$.

This is at present possible only between certain limits set out in table XII below. The first figure in each pair allocates the total colloid so far as possible to micelle; this cannot, of course, exceed the concentration of potassion or sodion, and any excess must necessarily be ascribed to neutral colloid. The second figure in each case makes the opposite assumption, allotting the total colloid to neutral colloid as far as possible. The maximum here is the total amount of undissociated soap obtained by subtracting the concentration of potassion or sodion from the total concentration of the solutions; any excess of colloid must then be recognised as ionic micelle. Table XII includes previous data for the case of potassium laurate at 90° for comparison. Results are expressed in mols. per 1000 grams of water.

TABLE XII.

Measured Limits of Concentration of Constituents of Soap Solutions.

N_w .	Neutral colloid, $(\text{KP})_x$	Micelle, $\text{P}_n^{(1)}$	Simple ion, P^{\cdot}	Simple undissociated KP^{\cdot}	Cation. K.
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Potassium Octoate at $0-18^\circ$.

1.0	0.00—0.14	0.14—0.00	0.35—0.50	0.50—0.35	0.50
2.0	0.31—1.13	0.82—0.00	0.04—0.82	0.82—0.04	0.82

Potassium Laurate at $0-18^\circ$.

0.1	0.01—0.04	0.03—0.00	0.00—0.03	0.06—0.03	0.03
0.2	0.06—0.13	0.07—0.00	0.00—0.07	0.07—0.01	0.07
0.4	0.24—0.26	0.14—0.11	0.00—0.03	0.03—0.00	0.14
0.5	0.30—0.32	0.18—0.16	0.00—0.02	0.02—0.00	0.18
0.6	0.36—0.39	0.21—0.18	0.00—0.03	0.03—0.00	0.21
1.0	0.60—0.64	0.36—0.32	0.00—0.04	0.04—0.00	0.36
2.0	1.21—1.34	0.66—0.53	0.00—0.06	0.13—0.07	0.66

Potassium Laurate at 90° .

0.2	0.00	0.00	0.10	0.10	0.10
0.5	0.00—0.22	0.22—0.00	0.04—0.26	0.24—0.02	0.26
1.0	0.33—0.48	0.52—0.37	0.00—0.15	0.15—0.00	0.52
2.0	1.00—1.11	0.89—0.78	0.00—0.11	0.11—0.00	0.89

TABLE XII. (continued).

Measured Limits of Concentration of Constituents of Soap Solutions.

N_m	Neutral colloid, (KP) _z	Micelle, $P_m^{(c)}$	Simple ion, P_s	Simple undissociated KP.	Cation. K.
<i>Potassium Oleate at 0—18°.</i>					
0.1	0.05—0.08	0.02—0.00	0.00—0.02	0.02—0.00	0.02
0.2	0.14—0.15	0.05—0.04	0.00—0.01	0.01—0.00	0.05
0.4	0.28—0.29	0.11	0.00	0.00	0.11
0.5	0.35—0.36	0.14	0.00	0.00	0.14
0.6	0.41—0.43	0.17—0.16	0.00—0.01	0.01—0.00	0.17
<i>Sodium Oleate at 0—18°.</i>					
0.2	0.15—0.16	0.04—0.02	0.00—0.01	0.01—0.00	0.04
0.4	0.32	0.08	0.00	0.00	0.08

An inspection of the data in table XII reveals that in the cases of the oleates and the more concentrated solutions of the laurates, the limits of concentration of each constituent are narrowly defined. These solutions consist almost entirely of colloid, together with potassium or sodium. There is more than twice as much neutral colloid, (KP)_z, as of agglomerated ions, $P_m^{(c)}$; in these potassium soaps and in sodium oleate there is four times as much (NaP)_z as of $P_m^{(c)}$, whereas at 90° the proportion varied between 3.2 and nearly equal amounts.

Once more the difference between potassium and sodium soaps asserts itself, a difference that is evidence for the inclusion of the neutral colloid in the micelle, since otherwise the micelle must be of identical composition in the two cases. Although there is the same total amount of colloid in both cases, the sodium soap contains only about half as much micelle.

Comparison with solutions at higher temperatures shows that there is more neutral colloid present at low temperatures, presumably in the micelle, and possibly in the same way that there is also greater hydration at the lower temperature. This accords also with the abnormally high temperature-coefficient of conductivity.

Comparison with Results of Dew-point Measurements at 20°.

We have carried out a few dew-point measurements at 20° for comparison, employing the method previously described. The data

are given in table XIII. It will be noticed that the data agree exactly with the most accurate of the freezing-point data; the method is applicable at all temperatures, and therefore to all soap solutions.

TABLE XIII.

*Measurements of Lowering of Dew Point of Soap Solution.**

Soap.	N _m .	Tem- perature.	Lowering.	Crystal- loid.	"i."
Potassium chloride	1.0N	20°	0.58°	1.99	1.99
" laurate	0.2	20	0.04	0.14	0.70
" octoate	3.0	20	0.70	2.41	0.99
" oleate	0.6	20	0.07	0.24	0.40
0.2 Potassium laurate } 0.6 " oleate }	—	20	0.12	0.41	0.51
Ammonium laurate	1.0N	20°	0.17°	0.593	0.583
" " 	0.5	20	0.08	0.275	0.55
" palmitate ...	1.0	20	0.06	0.206	0.21
" " 	1.0	90	0.13	0.277	0.28

The complicated effect possible when soaps are mixed in solution has been discussed elsewhere. In the case of the mixture in table XIII, 0.6N in respect of oleate and 0.2N in respect of laurate, the total concentration of crystalloid is 0.41N, as compared with 0.38N, the sum of that of the constituents separately. The conductivity of the mixture is also 5 per cent. above that of the constituents, so that most of this increase may be attributed to formation of mixed ionic micelle.

Ammonium Soaps.

The study of ammonium soap prepared from palm-kernel oil (which is largely laurate with some higher constituents) by Goldsmidt and Weismann (*Kolloid Zeitsch.*, 1913, **12**, 18) has given very interesting results. Like the potassium soaps, they exhibit fairly high conductivity, which in this case cannot possibly be due to products of hydrolysis. The conductivity curve differs greatly from those of sodium and potassium soaps in that it rises steadily with concentration from 0.2N- up to 1.0N-solution by about 38 per cent. The rise is rapid at first, then more gradual. Dilute solutions were not measured. The rise is accompanied by an increase in viscosity of several hundred-fold. All these solutions are appreciably hydrolysed, as is shown by the increase in conductivity effected by addition of excess of ammonia, which in itself is a poor conductor.

These results can be interpreted as showing that the simple fatty

* Measurements by M. E. L.

ion existing in more dilute solutions is being replaced in more concentrated solutions by the ionic micelle, which is a better conductor. This is quite in accord with our conclusions, but the micelle in concentrated solutions must conduct as well as a good conducting ion, such as potassium.

Some dew-point measurements of ammonium soaps are given in the lower half of table XIII. The solutions were prepared from pure fatty acids. It was not considered necessary to correct them for the effect of the partial pressure of the ammonia, as it was evidently too small.

In warm weather, the *N*- and *N*/2-laurates were quite clear solutions showing none of the usual appearances of soap solutions except that they gave a very good lather. On cooling, the *N*/2-laurate solution deposited feathery, crystal-like flakes; the *N*-solutions did not do this, but in very cold weather they set to a semi-transparent jelly similar to a potassium soap. The *N*/2-palmitate was somewhat similar, but the *N*-solution was practically solid at all temperatures, and resembled solid white foam.

A glance at the results shows that, independent of the temperature, there is a very large difference between ammonium laurate and palmitate—very much greater than that observed in potassium soap solutions. The total crystalloid in ammonium laurate is nearly 50 per cent. greater than in potassium laurate, whereas in ammonium laurate it is much less than in ammonium palmitate. An appreciable fraction of the total crystalloid will be undissociated ammonia.

Further investigation would evidently be well repaid, particularly if pure fatty acids were used for making the solutions and hydrolysis were avoided, as suggested above. Enough has been presented to show that the relationships agree with our general conception of colloidal electrolytes.

General Conclusions and Summary.

The theory of colloidal electrolytes defined by one of us receives further confirmation from the measurements of conductivity, freezing point, and vapour pressure of soap solutions at the ordinary temperatures here communicated.

The general theory is based on the conception, justified on mechanical grounds, that ions may be aggregated to form the nucleus of a colloidal particle, termed the ionic micelle, whilst retaining their equivalent electrical charges. Thus the ionic micelle exhibits conductivity as well as mobility even greater than the ions contained in it.

In the case of soap solutions, such as those of potassium oleate, the ionic micelle in concentrated solutions exhibits an equivalent conductivity three times greater than the oleate ion and equal to that of the potassium. Its general formula may be taken as $(\text{KOI})_x \cdot (\text{OI})_n^{m'} \cdot (\text{H}_2\text{O})_m$, the amount of water of hydration involved being least in concentrated solutions and at higher temperatures. The change in hydration explains the abnormal temperature-coefficient of conductivity.

The formation of colloid, in the case of higher soaps, is so complete at the ordinary temperature that in all ordinary solutions the only other constituent is the potassium, sodium, or ammonium, as the case may be. In dilute solutions, the soaps become simple crystalline salts, and hydrolysis becomes appreciable.

No other representative of this very numerous and important group of substances has yet been completely investigated, but the data available for such instances as the silicates, tellurates, dyes, proteins, salts of alkaloids, gelatin, or casein, etc., agree with the requirements of the theory, which affords a fresh interpretation and reconciliation of the results.

In conclusion, we desire to express our thanks to the Colston Society of the University of Bristol for substantial grants towards the purchase of materials and apparatus.

CHEMICAL DEPARTMENT,

THE UNIVERSITY, BRISTOL.

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CXX.—*The Degree of Hydration of the Particles which Form the Structural Basis of Soap Curd, Determined in Experiments on Sorption and Salting Out.*

By JAMES WILLIAM MCBAIN and MILLICENT TAYLOR.

In 1911 we published experiments on the salting out of sodium palmitate by sodium hydroxide, the results of which appeared to us highly remarkable (*Zeitsch. physikal. Chem.*, 1911, **76**, 199, table IX). When the sodium palmitate was salted out, the clear solution that remained as mother liquor, or lye, contained a higher concentration of sodium hydroxide than before.

The explanations advanced were either that the curd which was salted out contained some acid sodium palmitate, or that very

pronounced negative sorption had occurred; and further experiments to decide this were outlined.

It is the object of this communication to present the results of the first of a series of investigations which show that salted out sodium palmitate is hydrated, and that the curd as a whole consists of this hydrated solid together with entangled or enmeshed mother liquor.

It is impossible to elucidate this problem merely by the direct analysis of the curd, since the curd contains a quantity of concentrated lye mechanically entangled, and yet cannot be washed.

If acid soap were present, it would nevertheless be entirely masked by the large amount of free alkali in the solution clinging to it. Methods had to be devised for distinguishing the water chemically or physically combined (sorbed) from that of the enmeshed solution, thus affording a knowledge of the composition of the curd itself.

In carrying out the present experiments the concentration of the lye before and after salting out was determined, and this was supplemented by a complete analysis of the wet curds. The calculation is based upon the assumption that the sodium hydroxide is not appreciably sorbed by the hydrated curd. As will be shown, this leads to values which are only slightly less than the true degree of hydration. Methods of preparation employed and precautions observed were those previously described.

The Method of Calculation of Hydration from Analysis of Lyes.

If a system is made up by taking 1 mol. of sodium palmitate (NaP) and 1000 grams of water and 2 mols. of sodium hydroxide (thus 2.000 weight-normal, N_w) and the curd separates out quantitatively with, say, a composition corresponding with $\text{NaP}_5\text{H}_2\text{O}$, 5 mols. of water will have been abstracted from the lye. The removal of $5 \times 18.02 = 90.1$ grams of water from the 1000 grams originally present will have resulted in an increase of the weight-normality of the solution of sodium hydroxide from the value $N = 2.000$ to a normality N' , where

$$N' = \frac{1000}{1000 - 90.1} N.$$

Hence, in general, if W is the weight of water abstracted,

$$W = 1000 \left(1 - \frac{N}{N'} \right) \text{grams.}$$

If the weight-normality of the original sodium palmitate had been

N_s , the hydrate or sorbed water abstracted by N_s mols. of sodium palmitate would have been

$$\frac{W}{18.02 \times N_s} \text{ mols. of water,}$$

or

$$\frac{1000}{18.02 \times N_s} \left(1 - \frac{N}{N_s}\right) \text{ mols. of water to one of NaP.}$$

The residual sodium palmitate in solution in the lye amounted to only a few ten-thousandths normal, which does not affect the results.

Actually in most of the experiments, pure palmitic acid was weighed into a large silver tube and a measured volume of a concentrated solution of sodium hydroxide was added. After sealing with pure silver the tube was placed in a thermostat at about 90° and shaken during periods ranging from ten days to three months. The contents were then filtered through perforated silver foil at 90°. In carrying out the calculation outlined above, the water formed by the chemical reaction between the palmitic acid and the sodium hydroxide was taken into account, and volume was converted into weight-normality.

Hydration Results from Analysis of Lyes.

Table I presents the data of ten experiments in which sodium palmitate was salted out by sodium hydroxide. The first column contains the number of the experiment for further reference; the second, the total amount, in mols., of palmitate in 1000 grams of water, calculated as sodium palmitate; the third, the amount of sodium hydroxide in excess; the fourth, the time allowed for interaction; the fifth, the weight-normality of the sodium hydroxide in the lye after the experiment; the sixth, the amount of sorbed water to 1 mol. of sodium palmitate. In experiment 3 (a) previously prepared pure sodium palmitate was added to the hydroxide; in all other cases palmitic acid was added direct.

TABLE I.

Hydration of Sodium Palmitate Curds at 90°.

No. of expt.	Original charge.		Time shaken.	Lye, NaOH N.	Hydration: mols. H ₂ O to 1 NaP.
	NaP. N_s .	NaOH. N.			
1a	0.9823	2.9470	10 days	3.119	3.1
10	0.9939	2.9816	4 weeks	3.2189	3.7
Mean hydration=3.4 H ₂ O.					

TABLE I. (continued).
Hydration of Sodium Palmitate Curds at 90°.

No. of expt.	Original charge.		Time shaken.	Lye, NaOH N.	Hydration: mols. H ₂ O to 1 NaP.
	NaP. N.	NaOH. N.			
1	0.9608	1.9215	4 months	2.084	4.5
3	0.9608	1.9216	3 "	2.1004	4.9
6	0.9337	1.8675	10 weeks	2.042	5.0
7	0.4949	1.7919	10 "	1.898	6.3
Mean hydration = 5.2 H ₂ O.					
3a	0.5021	1.5065	14 days	1.611	7.2
2a	0.495	1.485	10 "	1.596	8.0
11	0.5002	1.5006	4 weeks	1.566	4.7
12	0.5145	1.589	4 "	1.686	6.2
Mean hydration = 6.5 H ₂ O.					

The results recorded in table I show clearly that there is a definite amount of combined water in each case, and that this depends on the concentration of sodium hydroxide present in equilibrium with the curd. Thus for 3.0, 1.9, and 1.5*N*-sodium hydroxide solutions the hydration is 3.4, 5.2, and 6.5 mols. of water to 1 mol. of sodium palmitate. In other words, halving the concentration of the lye has doubled the degree of hydration.

Of course, if some sodium hydroxide also is combined in the curd, the above numbers have to be slightly increased to give the true hydration values.

The result found for curd in the presence of 1.9*N*-sodium hydroxide is confirmed by an analysis of the curd itself. One hundred grams of curd contained 57.66 grams of sodium palmitate, 1.681 grams of sodium hydroxide, and 40.66 grams of water; or, to 1 mol. of sodium palmitate, 0.2027 mol. of sodium hydroxide and 10.89 mols. of water. Since the lye was shown to be 1.898*N*-sodium hydroxide, 5.93 mols. of water are to be regarded as solvent (enmeshed lye). This leaves 5.0 mols. of water of hydration to 1 mol. of sodium palmitate, as compared with the mean result, 5.2 mols., given in table I. Again, it is of interest to note that this curd contained about equal amounts of enmeshed lye and combined water.

Two further results are given in table II. Here the solution employed for salting out contained 2*N*-sodium chloride together with *N*/2-sodium hydroxide and previously prepared sodium palmitate.

The headings of the columns are as in table I, except that a

column giving the original normality of sodium chloride has been inserted after the third.

TABLE II.

Hydration of Sodium Palmitate at 90°.

No. of expt.	Original NaP.	Charge NaOH	NaCl.	Time shaken.	Lye NaOH.	Hydration mols. H ₂ O.
15	1.100	0.5069	2.000	2 weeks	0.5508	4.4
16	1.000	0.5069	2.000	14 days	0.5508	4.4

Mean hydration = 4.4 H₂O.

This result, 4.4H₂O to 1NaP, where the lye is 2.5*N* altogether, agrees excellently with the values in table I, and would make it appear that the hydration of the curd may be governed more by the concentration of the lye than by the nature of the salt employed in salting out. If this proves to be the case it will only be necessary to ascertain the molar concentration of soap lye in order to measure the hydration of commercial soap curds, once a standard value for each type has been obtained.

Results with sodium stearate are given in table III, showing that with 1.4*N*-sodium hydroxide the mean hydration is about 4.3H₂O, as compared with 6.5H₂O for the palmitate.

TABLE III.

Hydration of Sodium Stearate Curd at 90°.

No. of expt.	Original Na stearate.	Charge NaOH.	Time shaken.	Lye NaOH.	Hydration mols. H ₂ O.
13	0.4679	1.404	46 days	1.444	3.3
14	0.4679	1.404	48 "	1.469	5.3

Mean hydration = 4.3 H₂O.

The Effect of great Pressure on the Hydration of Soap.

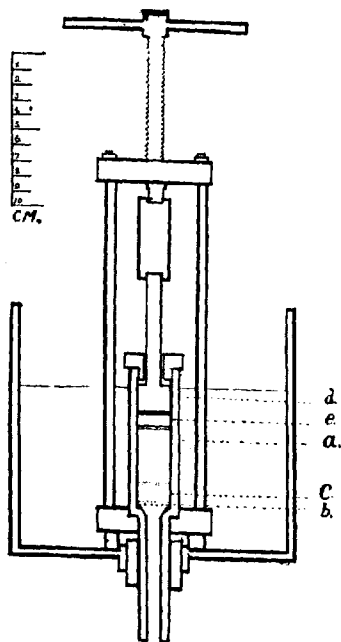
In order to leave no loophole for the alternative explanation of the phenomena here considered, experiments were carried out in which the curd was subjected to a pressure of hundreds or thousands of atmospheres during filtration. The lye filtering through was, of course, concentrated sodium hydroxide, and if the solid part of the curd really contained acid sodium palmitate, and if the separation from the curd was carried far enough, analysis of the residual curd must show a direct deficiency of alkali. However, we found that the curd was always alkaline, no matter how extreme the pressure or how much lye had been forced out. The only observed effect of applying pressure to the curd, whilst allowing the lye to escape, was to diminish the amount of hydration.

The press employed, together with the thermostat in which it was

fixed, is sketched in cross-section in the figure. The filter bed consisted essentially of sugar-carbon previously treated with lye, but arranged so as to avoid contact with the soap curd as far as possible.

The filtration was carried out in the steel tube *a*, fitted with a perforated steel filter disk, *b*.

On the top of this disk was a sheet of nickel gauze, and above



Press employed for diminishing the hydration and imbibition of soap curd.

that again a layer of perforated silver foil. The carbon bed, *c*, some 1–1.5 cm. in depth, rested on the foil and was covered with two more layers of the perforated silver foil. Before use the whole bed was moistened with lye and made thoroughly compact by pressure from the piston *d*.

The soap curd from which the lye had been rapidly filtered, through a silver cone, at 90°, was transferred to the filter and covered with two layers of perforated silver foil. Between this and

the steel piston was inserted a hollowed out, thick-walled rubber washer of the form used in a Bramah press. Pressure was applied through the screw by means of a double set of levers, about 80 cm. in length.

The sample of curd for analysis was taken from the centre of the block of hard curd left in the press. In satisfactory experiments it contained no carbon. Various methods were employed in the analysis, but only the one found most convenient is here described.

The curd was dissolved in neutral, boiled-out 80 per cent. alcohol containing phenolphthalein. The solution was titrated with *N*/10-sulphuric acid, the alcohol evaporated, and excess of *N*-sulphuric acid added. After decomposition of the soap had been completed by alternate heating and cooling, the solid palmitic acid was collected. The filtrate was titrated to ascertain the amount of sodium palmitate which had been present. In many cases the palmitic acid was determined directly by weighing or by titration in alcoholic solution. Water was always obtained by difference. The method of calculation was usually that illustrated by the curd analysis accompanying table I above. This is termed "mixed" calculation in the table above.

In a few cases, however, the concentration of lye after salting out was not determined. Here the amount of lye and its concentration were calculated from the analysis of the curd by successive approxi-

TABLE IV.

Hydration of Curds after Great Pressure at 90°.

No. of expt.	Original charge.		Curd composition: 100 grams of curd contain			Method of calculation.	Hydration: moles. H ₂ O: to 1NaP.
	NaP. <i>N.</i>	NaOH. <i>N.</i>	NaP.	NaOH.	H ₂ O.		
10	0.994	2.98	83.644	0.899	15.457	"Mixed"	1.547
4	0.997	1.99	77.580	1.154	21.266	"Curd"	1.42
1	0.961	1.92	(73.850	1.286	24.864)	"Mixed"	2.0
			(74.424	1.383	24.193)		1.6
2	0.961	1.92	(69.99	1.021	28.994)	"Curd"	3.6
			(67.23	1.306	31.479)		3.5
			(77.51	1.153	21.342)		(1.3 pressed on tile)
3	0.961	1.92	66.146	1.235	32.619	"Mixed"	4.3
6	0.934	1.87	(68.404	1.329	30.267)	"Mixed"	3.3
			(67.616	1.314	31.070)		3.4
			(81.913	2.084	16.003)		— 1.8 (pressed on tile)
7	0.495 Sodium stearate	1.79	73.804	0.785	25.411	"Mixed"	3.2
13	0.468	1.404	70.682	1.227	28.091	"Mixed"	1.6
14	0.468	1.404	72.916	0.905	26.179	"Mixed"	2.5

mations based on the hypothesis that all excess of hydroxide was contained in the lye and not in the curd proper. As may be shown theoretically, this leads to a perfectly defined result for the value of the hydration. This we term the pure "curd" calculation.

The results for sodium palmitate salted out by sodium hydroxide are given in table IV. The pressure was different in each case, since it depended on the condition of the filter bed, pressure being applied until the curd began to be forced through. (In one or two cases some carbon was mixed with the curd.) Several samples at different levels were taken for analysis in some of the experiments. Table V gives similar data for the pressed curds of Experiments 15 and 16 of table II.

TABLE V.

No. of expt.	Curd composition: 100 grams contain			Method of calculation.	Hydration: mols. H ₂ O to 1 NaP.
	NaP.	NaOH.	NaCl.		
15	80.01	0.144	0.761	"Mixed"	2.2
16	80.43	0.160	0.922	"Mixed"	2.2

On examining the results of tables IV and V it appears that the very great pressure to which the curds were subjected while in contact with residual lye lowers the degree of hydration to about half of that of the unpressed curd. This is in accordance with the recognised property of colloids that the swelling pressure increases enormously as the solvent is removed, although the pressures here employed far transcend those hitherto investigated.

The most effective way of dehydrating soap curd is to press it on a porous tile, thus making use of the swelling pressure of kaolin to abstract the water. Curds from Experiments 2 and 6 so treated and the composition calculated as before, gave values for apparent hydration of 1.3 and -1.8 mols. of water respectively; this appears to show that the residual lye had also been greatly concentrated in the process owing to hydroxide being left when the water was absorbed.

Summary.

Marked negative sorption of sodium hydroxide occurs when soap is salted out by sodium hydroxide in concentrated solution.

From the extent of this effect the amount of water contained in the solid part of the curd, as distinguished from the entangled lye clinging to it, may be deduced. Soap curd is thus shown to be a mechanical mixture of hydrate (or sorption compound) and unmeshed lye.

The degree of hydration varies with the concentration of lye as follows:

Lye.	Sorption compound.	Percentage of fatty acid.
3.0 <i>N</i>	NaP,3-2H ₂ O	76.28
2.5	NaP,4-4H ₂ O	71.67
1.9	NaP,5-2H ₂ O	68.89
1.5	NaP,6-5H ₂ O	64.81

Extreme pressure lowers the degree of hydration considerably.

In conclusion, we have pleasure in thanking the Colston Society of the University of Bristol for a generous grant towards the purchase of materials and apparatus.

THE CHEMICAL DEPARTMENT,
BRISTOL UNIVERSITY.

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Organic Chemistry.

The Action of Cuprous Chloride with Compounds containing the Trichloromethyl Group. HOWARD WATERS DOUGHTY (*J. Amer. Chem. Soc.*, 1919, **41**, 1129—1131).—As an outcome of his work on the hydrolysis of organic haloids and the corrosion of metals (A., 1918, i, 57), the author recommends the following procedure as a test for the presence of compounds containing the CCl_3 or CBr_3 groups. A few milligrams of the substance are placed in a stoppered vessel of 10—15 c.c. capacity, which is then filled with concentrated ammonia solution. About 0.5 gram of powdered cuprous chloride is then added, and the vessel is quickly closed to exclude air, and shaken. The deep blue colour of the cupric-ammonia complex develops in a minute or two if a trichloro- or tribromo-methyl group is present. Carbon tetrachloride behaves in the same way, but hexachloroethane does not respond to the test. J. C. W.

Preparation of Trichloroethylene from Tetrachloroethane. COMPAGNIE DES PRODUITS CHIMIQUES D'ALAIS ET DE LA CAMARGUE (Eng. Pat., 132755).—The conversion of *s*-tetrachloroethane into trichloroethylene may be effected by ammonia in aqueous solution provided that a sufficient time be allowed for the reaction. A mixture of equal parts of water and tetrachloroethane is treated in a vessel provided with a reflux condenser with a current of ammonia gas sufficiently violent to agitate the mass. The reaction takes place slowly in the cold, and is accelerated by heating at 60—70°; it is complete in two hours if the trichloroethylene is removed as it is formed by extracting it with an excess of ammonia gas and adjusting the temperature of the condenser in accordance with this excess. The reaction may also be conducted in an autoclave by heating two parts of tetrachloroethane with two parts of an aqueous solution of ammonia (D 0.91) at 140—170° for three hours. The use of aqueous ammonia is simpler and more economical than that of alcoholic ammonia, and the yield of trichloroethylene is 92—96% of the theoretical. J. F. B.

Vapour Pressure of Tetranitromethane. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1919, **41**, 1336—1337).—The vapour pressure of tetranitromethane has been determined by a static isothermographic method, previously described (A., 1910, ii, 1036), over the temperature range 40—125.7°. The following values were obtained in mm. of mercury: 40°, 26.6; 45°, 34.4; 50°, 44.2; 55°, 56.1; 60°, 70.6; 65°, 88.1; 70°, 109; 75°, 134; 80°, 164; 85°, 199; 90°, 239; 95°, 286; 100°, 339; 105°, 400; 110°, 470; 115°, 550; 120°, 640; 125°, 743; and 125.7°, 760. Using the vapour-pressure curve in the way suggested by Hillebrand (A., 1915, ii, 416), the value 13.9 is obtained for the entropy

of vaporisation divided by R at the temperature (70°) at which the concentration of the vapour is 0.00507 mol. per litre. Assuming that the vapour is normal, this would indicate slight, if any, association or abnormality in the liquid at this temperature.

J. F. S.

The Oxidation of Ethyl Alcohol by means of Potassium Permanganate.

WILLIAM LLOYD EVANS and JESSE E. DAY (*J. Amer. Chem. Soc.*, 1919, **41**, 1267—1285. Compare A., 1916, i, 362).—The series of experiments described in this communication are designed to elucidate the following points: (1) the nature of the products formed when ethyl alcohol is oxidised by neutral or alkaline permanganate at different temperatures; (2) the effect of changing the temperature and altering the initial concentration of alkali, and the combined effect of varying these factors; (3) the mechanism of the oxidation. The analytical methods are fully described, and a simple apparatus is illustrated in the text by means of which clear samples of the filtrate from the oxides of manganese can be obtained without exposure to the carbon dioxide of the atmosphere. In the experiments, just sufficient of a 9.21% solution of alcohol was added to 30 grams of 100% permanganate dissolved in 1000 c.c. of various solutions of potassium hydroxide to cause reduction.

The results are reproduced in a set of curves, as follows: (A) The weights of alcohol required to reduce a constant weight of permanganate at 25° , 50° , 75° , and 100° are plotted against the different concentrations of alkali, and the curves show that beyond a concentration of about 100 grams per litre, the proportion of potassium hydroxide is immaterial, whilst up to this point both increase of temperature and increased alkalinity accelerate the reduction. (B) The quantities of the oxidation products, acetic, oxalic, and carbonic acids, given by 0.1 gram-mol. of alcohol are plotted against concentrations of alkali for the four different temperatures. In neutral solutions the sole product is acetic acid, and in the experiments at 100° it is still only acetic acid as long as the concentration of alkali is less than 0.461 gram per litre. With the increase in the amount of potassium hydroxide, however, up to the maximum effect (100 grams per litre), the production of acetic acid diminishes and that of oxalic acid and carbon dioxide increases. (C) The quantities of the three oxidation products are separately plotted against alkali concentrations for the four temperatures. With increase of temperature, it appears that the yield of acetic acid falls, and the quantities of oxalic acid and carbon dioxide increase.

Another set of curves shows the connexion between the logarithms of the quantities of acetic acid produced and the logarithms of the initial concentrations of potassium hydroxide. These curves may be reproduced by the equation $y = B_1 x^a$, where y is the concentration of the acetic acid, x is the concentration of the alkali, a is the tangent of the line, and B is a constant, whence $\log y = \log B - a \log x$. From the values of B and a for the four

temperatures, it is possible to calculate the maximum concentration of alkali which will still permit of a theoretical yield of acetic acid. These are as follows:

Temperature.....	25°	50°	75°	100°
KOH, grams per litre...	2.55	1.19	0.655	0.460

That is, it is possible to obtain acetic acid only, no matter what the temperature, if the concentration of alkali is kept below these limits. On the other hand, if the tangents of the acetic acid log. curves (the above values of a) are plotted against temperature, a straight line is obtained which, if continued, meets the point at which $a=0$ on an axis of Y corresponding with -25° ; this means that below this temperature the yield of acetic acid would be quantitative, no matter what the concentration of potassium hydroxide.

The mechanism of the formation of oxalic acid and carbon dioxide is discussed. The experiments support the views of other workers, namely, that the oxalic acid is not formed from acetic or formic acid, but from a derivative of acetaldehyde.

J. C. W.

The Temperature of Critical Solution of a Ternary Mixture as a Criterion of Purity of *n*-Butyl Alcohol. The Preparation of Pure *n*-Butyl Alcohol. KENNEDY JOSEPH PREVITÉ ORTON and DAVID CHARLES JONES (T., 1919, 115, 1194—1203).

The Preparation of $\alpha\beta$ -Dichloroethyl Ether. E. A. WILDMAN and HAROLD GRAY (*J. Amer. Chem. Soc.*, 1919, 41, 1122—1123).—Dichloroethyl ether may be obtained by the direct chlorination of ethyl ether (Fritsch and Schumacher, A., 1894, i, 485), but the operation is accompanied by two risks: (1) If the liquid is not well cooled at the outset, and the chlorine is admitted too rapidly, explosion may be caused by the inflammation of the ether vapour. This risk is lessened when the liquid is saturated with hydrogen chloride, and then the operation may be carried on rapidly. (2) Hydrogen chloride seems to form a super-saturated solution in ethyl ether, which may suddenly break out like a geyser; to obviate this, continuous, rapid agitation is necessary.

In order to get a pure product, b. p. $66-69^{\circ}/45$ mm., chlorination must be stopped when the density is 0.96. Starting with 800 grams of ethyl ether, this point is reached in about eighty-two hours, and the yield is about 375 grams.

J. C. W.

Action of Metallic Hydroxides and Oxides and Alkaline-earth Carbonates on Methyl Sulphates. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, 169, 534—537).—The behaviour of methyl sulphate in the presence of alkali hydroxides or alkaline earth oxides, hydroxides, or carbonates, depends to a large extent on the experimental conditions.

With potassium hydroxide in equimolecular proportions in methyl-alcoholic solution, methyl sulphate gives an almost quantitative yield of potassium methyl sulphate. A similar reaction occurs with calcium or barium hydroxide in the presence of a large excess of water. On the other hand, methyl sulphate may be distilled unchanged from barium or calcium oxide. With barium or calcium hydroxides in the absence of water, the action is $\text{Me}_2\text{SO}_4 + \text{M}(\text{OH})_2 = \text{MSO}_4 + \text{Me}_2\text{O} + \text{H}_2\text{O}$.

With cuprous, lead, mercuric, or silver oxides the action is, for example, $\text{Me}_2\text{SO}_4 + \text{Cu}_2\text{O} = \text{Cu}_2\text{SO}_4 + \text{Me}_2\text{O}$.

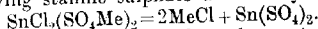
Methyl sulphate may be distilled unchanged from a small amount of an alkaline earth carbonate, but if kept at 140° for some time in the presence of the carbonate, it is decomposed according to the equation $\text{Me}_2\text{SO}_4 + \text{MCO}_3 = \text{MSO}_4 + \text{CO}_2 + \text{Me}_2\text{O}$, the reaction being slow.

W. G.

The Action of Stannic Chloride on Methyl Sulphate.

CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1919, 169, 618—620).

—Stannic chloride acts on methyl sulphate in two stages, which may overlap, methyl chloride being, in each case, the gas liberated. If the action takes place at the ordinary temperature, it is represented by the equation $\text{SnCl}_4 + 2\text{Me}_2\text{SO}_4 = 2\text{MeCl} + \text{SnCl}_2(\text{SO}_4\text{Me})_2$, the methosulphate of stannyl chloride being obtained as a white, amorphous solid. At higher temperatures, this compound is decomposed, giving stannic sulphate and methyl chloride,



The use of an excess of methyl sulphate does not modify the sense of the complete reaction, but seems to favour the second stage.

The methosulphate of stannyl chloride is decomposed by aqueous potassium hydroxide, giving stannic hydroxide, potassium chloride, and potassium methyl sulphate.

W. G.

Methionic [Methanedisulphonic] Acid and its Applications in Syntheses. G. SCHROETER [with G. KOCH, G. HERZBERG, TH. MARIAM, W. SONDAG, C. FRESSENIUS, W. ROTHMANN, A. GLUSCHKE, R. VON BUTLAR-BRANDENFELS, W. DORN, DIESSELHORST, E. KINDERMANN, EMMY SCHROETER, and O. CARLÉ] (*Annalen*, 1919, 418, 161—257).—Portions of this paper have been published during the last twenty-two years.

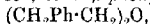
A description is given of the preparation of methanedisulphonic acid from acetylene (350—400 grams) and fuming sulphuric acid (65—70% SO_3) (about 6 kilos.) through the barium salt (700 grams of the salt from 1 kilo. of acid). The presence of phenol among the by-products, recorded by Berthelot in 1869, has been confirmed, and an explanation of its formation is suggested.

The reactions of methanedisulphonic acid have been thoroughly studied in the expectation of finding for it synthetic uses similar to those of malonic acid.

Improvements in the method of preparing methyl methanedisulphonate from the silver salt and methyl iodide (Schroeter and Herzberg, A., 1905, i, 851) are described; the ethyl ester has

been obtained in flattened needles, m. p. 28—29°. An attempt to prepare the benzyl ester from the silver salt and benzyl chloride in boiling benzene resulted in the formation of hydrogen chloride and diphenylmethane, the silver salt acting (so also does silver sulphate) simply as a catalyst.

Alkyl methanedisulphonates can also be prepared from alcohols and methanedisulphonyl chloride, but the method is not a suitable one, because, unless the violence of the reaction is moderated by the presence of a suitable diluent (ethyl ether), the resulting esters decompose into methanedisulphonic acid and ethers. The tendency of alkyl methanedisulphonates to decompose into methanedisulphonic acid and ethers (Schroeter and Sondag, A., 1908, i, 497) has been utilised in the preparation of heptyl ether, b. p. 126—127°/8 mm., D^{20}_D 0.8056, from heptyl alcohol and methanedisulphonyl chloride at 145°, of *di-β-phenylethyl ether*,



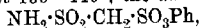
b. p. 175—176°/8 mm., D^{15}_D 1.0178 (a little styrene is also formed), from *β-phenylethyl alcohol*, and of *cyclohexene* from *cyclohexanol* in a similar manner. Aryl methanedisulphonates, on the contrary, are very stable compounds, and must be heated with a concentrated solution (50%) of alkali hydroxide to decompose them into phenols and methanedisulphonic acid. In consequence of the acidity of the methylene group between the two $\cdot\text{SO}_3\text{Ar}$ groups, the aryl esters dissolve in concentrated aqueous ammonia and in dilute solutions of alkali hydroxides. They resemble the phenols in their antiseptic and bactericidal actions. *Phenyl methanedisulphonate (methionol)*, $\text{CH}_3(\text{SO}_3\text{Ph})_2$, prepared from methanedisulphonyl chloride and phenol (4 mols.) in boiling toluene, forms colourless needles, m. p. 82°; the *sodio-* and *potassio-*derivatives, $\text{CHNa}(\text{or K})(\text{SO}_3\text{Ph})_2$, are crystalline, and the *argento-*derivative is a colourless powder. The *dibromo-*derivative, $\text{CBr}_2(\text{SO}_3\text{Ph})_2$, forms colourless crystals, m. p. 58—59°. The *o-*, *m-*, and *p-tolyl* esters, $\text{CH}_3(\text{SO}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2$, form crystals, m. p. 84°, 56°, and 84° respectively, whilst the *guaiacol* and *catechol* esters have m. p. 90° and 190° respectively.

Methanedisulphonyl chloride (Schroeter and Sondag, *loc. cit.*) has been obtained in two modifications. The liquid form usually obtained, m. p. 8°, D^{15}_D 1.831, is converted under conditions which have not yet been definitely ascertained into a second modification, long needles or prisms, m. p. 36—37°; the liquid form is converted into the solid by inoculation with the latter, and the solid form is converted into the liquid by warming above the m. p.

Methanedisulphonyl chloride reacts abnormally with dry ammonia in chloroform solution and with diethylamine in ethereal solution, the products in both cases being, not the expected amides, but mixtures of substances the nature of which has not yet been ascertained. The reaction with aniline (4 mols.) in chloroform or benzene solution, however, is normal (Schroeter and Herzberg, *loc. cit.*). *Methanedisulphonacetanilide*, $\text{CH}_3(\text{SO}_3\cdot\text{NAcPh})_2$, m. p. 196—197°, *methanedisulphonbenzanilide*, m. p. 204—205°, *methanedisulphonmethylanilide*, colourless needles, m. p. 141.5—142.5°.

methanedisulphonethylanilide, m. p. 112—114°, *methanedisulphonanilidoethylanilide*, $\text{CH}_3(\text{SO}_2\text{NPh})(\text{SO}_2\text{NEtPh})$, m. p. 168°, *methanedisulphonphenetide*, $\text{CH}_3(\text{SO}_2\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, m. p. 221°, and its *methyl*, m. p. 132—133°, *ethyl*, m. p. 141—142°, and *aceto-phenetides*, m. p. 155°, *methanedisulphon-p-nitroanilide*, yellow needles, carbonising above 240°, and *methanedisulphondiphenylamide*, $\text{CH}_3(\text{SO}_2\text{NPh}_2)_2$, m. p. 228°, have been prepared. The preceding primary anilides are moderately strong acids forming sodium and barium derivatives and decomposing carbonates, but anilides which do not contain the NH-group are devoid of acid character, being insoluble in aqueous alkali hydroxide solution.

When a solution of phenyl methanedisulphonate in benzene saturated with ammonia is treated with an equal quantity of phenyl methanedisulphonate and the mixture is heated in a sealed tube for three hours at 130—140°, the *amide ester*,



crystals, m. p. 167°, is obtained; the same substance is also obtained by heating phenyl methanedisulphonate and carbamide in a sealed tube at 140—160°. When a solution of phenyl methanedisulphonate in benzene supersaturated with ammonia is heated in a sealed tube at 140—145°, *methanedisulphonamide*, $\text{CH}_3(\text{SO}_2\text{NH}_2)_2$, leaflets, m. p. 233°, is obtained; it forms *sodium* and *barium* derivatives and a *monobenzoyl* derivative, leaflets, m. p. 216°. *Methanedisulphonethylanilide*, $\text{CH}_3(\text{SO}_2\text{NHET})_2$, similarly prepared by means of a benzene solution of ethylamine, forms leaflets, m. p. 143—145°.

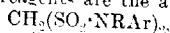
Methanedisulphonyl chloride reacts normally with esters of amino-acids in cold ethereal or chloroform solution. Thus, ethyl glycine and ethyl phenylglycine yield, respectively, *ethyl methanedisulphonaminoacetate*, $\text{CH}_3(\text{SO}_2\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, colourless needles, m. p. 113·5°, and *ethyl methanedisulphonanilinoacetate*, $\text{CH}_3(\text{SO}_2\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, colourless needles, m. p. 109—111°; the former is soluble in dilute alkali hydroxides and in aqueous ammonia, whilst the latter dissolves sodium or potassium with the evolution of hydrogen, and is hydrolysed by aqueous-alcoholic sodium hydroxide, yielding *methanedisulphonanilinoacetic acid*, $\text{CH}_3(\text{SO}_2\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, crystals with $2\text{H}_2\text{O}$, m. p. 110—112° (anhydrous).

Methanedisulphonphenylhydrazide, $\text{CH}_3(\text{SO}_2\text{NH}\cdot\text{NHPH})_2$, colourless needles, m. p. 118—119° (decomp.), and *methanedisulphonbenzoylhydrazide*, $\text{CH}_3(\text{SO}_2\text{NH}\cdot\text{NHBz})_2$, needles, m. p. 204—205° (decomp.), are prepared from methanedisulphonyl chloride and phenyl- and benzoyl-hydrazine, respectively, in ethereal or chloroform solution; the latter is soluble in aqueous alkali hydroxide.

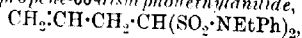
By introducing alkyl, aryl, and acyl groups in the methylene group, syntheses have been effected both with the esters and the amide derivatives of methanedisulphonic acid, but the replacement of the methylene hydrogen atoms by metals, and consequently also the course of the synthesis, depend on the nature of the

radicles attached to the SO_2 groups. The methyl and ethyl esters in ethereal or benzene solution react with the alkali metals, with the evolution of hydrogen, but the reaction becomes so slow before one atomic proportion of the metal has been added that syntheses attempted by this means follow a tedious and uncertain course; however, *ethane- $\alpha\alpha$ -disulphonic acid* and *propane- $\alpha\alpha$ -disulphonic acid* in the form of their *barium* salts have been obtained by the action of methyl and ethyl iodides, respectively, on a benzene solution of the methyl or ethyl methanedisulphonate to which potassium had been previously added. Aryl esters of methanedisulphonic acid form in aqueous solution stable salts with alkali hydroxides and with ammonia, but these salts, from some undetermined cause, are little suited for synthetic purposes in aqueous or alcoholic solution or suspension. When, however, the aryl esters are treated in an indifferent solvent with sodium, and the resulting solution or suspension is treated with alkyl haloid, methyl sulphate, or benzoyl chloride, reaction proceeds smoothly. *Phenyl ethane- $\alpha\alpha$ -disulphonate*, $\text{CHMe}(\text{SO}_2\text{Ph})_2$, *phenyl propane- $\alpha\alpha$ -disulphonate*, *phenyl propane- $\beta\beta$ -disulphonate*, crystals, m. p. 96–97°, and *phenyl butane- $\beta\beta$ -disulphonate*, an oil, have been thus prepared; also *p-tolyl ethane- $\alpha\alpha$ -disulphonate*, crystals, m. p. 57–60°, and *p-tolyl propane- $\beta\beta$ -disulphonate*, crystals, m. p. 88–91°, have been obtained, whilst the corresponding *o*-tolyl and *m*-tolyl esters are oily liquids.

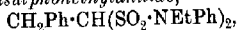
Numerous syntheses can be effected by means of the amide derivatives of methanedisulphonic acid. Any such derivative containing the NH group is inadmissible, however, because such substances form metallic derivatives containing the NNa group, and these lead to the production of *N*-substituted derivatives. The most efficient synthetic reagents are the alkylanilides,



particularly the very easily obtainable methanedisulphonethylanilide. These substances in warm benzene solution are treated with sodium or potassium, and the product is treated with an alkyl or acyl haloid. By these means, the CH_3 group of the methanedisulphonalkylanilides can be converted into CHMe , CHEt , $\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_3$, $\text{CH}\cdot\text{CH}_2\cdot\text{Ph}$, and $\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (*p*), but alkyl haloids of greater complexity react very slowly. Further, the remaining hydrogen atom of the preceding groups can be replaced by a methyl group, giving CMe_2 , CMeEt , etc., but not by an ethyl, allyl, or other radicle. Analogously to the preceding, the sodium derivatives, $\text{CHNa}(\text{SO}_2\cdot\text{NR}\cdot\text{Ar})_2$, react with the halogens, yielding derivatives containing the group CHCl , CHBr , or CHI ; from these, a dichloro-derivative, $\text{CCl}_2(\text{SO}_2\cdot\text{NR}\cdot\text{Ar})_2$, can be obtained, but not a dibromo- or diiodo-derivative. *Ethane- $\alpha\alpha$ -disulphonethylanilide*, $\text{CHMe}(\text{SO}_2\cdot\text{NEtPh})_2$, prisms, m. p. 150°, *ethane- $\alpha\alpha$ -disulphonethylanilide*, crystals, m. p. 95–96·5°, *propane- $\alpha\alpha$ -disulphonethylanilide*, prisms, m. p. 128–129°, and *p-phenetide*, $\text{CHEt}(\text{SO}_2\cdot\text{NEt}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, needles, m. p. 35–34·5°. Δ^2 -*propene- $\beta\beta$ -disulphonethylanilide*,



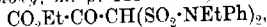
prisms, m. p. 120—121° (*dibromide*, needles, m. p. 103—106°), *β-phenylethane-αα-disulphonethylanilide*,



prisms, m. p. 104—106°, *β-p-nitrophenylethane-αα-disulphonethylanilide*, pale yellow, crystalline powder, m. p. 100—105°, *propane-ββ-disulphonethylanilide*, crystals, m. p. 130—132°, and the *-phenetidine*, m. p. 109°, *butane-ββ-disulphonethylanilide*, crystals, m. p. 114—116°, *Δ⁵-pentene-ββ-disulphonethylanilide*, m. p. 107° (*dibromide*, leaflets, m. p. 100—102°), and *α-phenylpropane-ββ-disulphonethylanilide*, m. p. 96·5—97°, are described.

Phenyl benzoylmethanedisulphonate, $\text{CHBz}(\text{SO}_2\text{Ph})_2$, crystals, m. p. 96°, and the corresponding *p-tolyl ester*, m. p. 91°, and *m-tolyl ester*, m. p. 102°, have been prepared.

The following acyl derivatives of methanedisulphonethylanilide are described: *formyl*, $\text{CHO}\cdot\text{CH}(\text{SO}_2\cdot\text{NEtPh})_2$, needles, m. p. 113—114°; *acetyl*, rhombic plates, m. p. 143—144°; *propionyl*, needles, m. p. 129—130°; *benzoyl*, m. p. 118—119°; *o-nitrobenzoyl*, prisms, m. p. 148—149°; *o-acetoxybenzoyl*, m. p. 152—153°; *carbethoxy*, m. p. 111—112°; and *ethoxalyl*,



plates, m. p. 103—105°. *Chloromethanedisulphonethylanilide*, $\text{CHCl}(\text{SO}_2\cdot\text{NEtPh})_2$, needles, m. p. 97—98°, the *bromo-derivative*, needles, m. p. 167—168°, the *iodo-derivative*, needles, decomp. 150—170°, and *dichloro-derivative*, m. p. 109—110°, are described.

Unlike malonic acid, methanedisulphonic acid is very stable towards mineral acids, so much so that the Carius method is inapplicable to the estimation of the sulphur. The aryl esters and anilides of the dialkylated acids, $\text{C}(\text{Alk.})_2(\text{SO}_3\text{H})_2$, are resistant to acid hydrolysis, but are smoothly decomposed by alcoholic alkalis under pressure in the sense of the equations: (1) $\text{CMe}_2(\text{SO}_3\text{Ph})_2 + 5\text{NaOH} = \text{OH}\cdot\text{CMe}_2\cdot\text{SO}_3\text{Na} + \text{Na}_2\text{SO}_3 + 2\text{Ph}\cdot\text{ONa}$ and (2) $\text{CMe}_2(\text{SO}_2\cdot\text{NEtPh})_2 + 3\text{NaOH} = \text{OH}\cdot\text{CMe}_2\cdot\text{SO}_3\text{Na} + \text{Na}_2\text{SO}_3 + 2\text{NHEtPh}$.

Sodium *β-hydroxypropane-β-sulphonate* thus obtained is not identical with the additive compound of acetone and sodium hydrogen sulphite.

Acyl derivatives of aryl esters or secondary anilides of methanedisulphonic acid are extraordinarily stable towards alkalis; the latter class of compound is decomposed by heating with mineral acids in the sense of the equation $\text{CHBz}(\text{SO}_2\cdot\text{NEtPh})_2 + 3\text{H}_2\text{O} = \text{CH}_2\text{Bz}\cdot\text{SO}_3\text{H} + \text{H}_2\text{SO}_4 + 2\text{NHEtPh}$. C. S.

Dehydration of Formic Acid Solutions. D. C. JONES (*J. Soc. Chem. Ind.*, 1919, **38**, 362—363r).—It is shown that, in spite of previous statements to the contrary, phosphoric oxide can be used satisfactorily for the dehydration of concentrated solutions of formic acid. The conditions to be observed are that the calculated quantity of phosphoric oxide necessary to combine with the water present in the formic acid be added gradually, the mixture being well cooled and shaken during the addition. The formic acid is then distilled under 15—18 mm. pressure, and can

readily be obtained up to 99.5% strength. When excess of phosphoric oxide is used, considerable decomposition of the formic acid occurs.

The concentration of dilute solutions of formic acid is limited by the formation of a constant boiling mixture containing 77% of acid by weight and boiling at 107.1°. The composition of the constant boiling mixture is found to vary to a considerable degree with the pressure, decreasing in formic acid content with diminishing pressure, until at 43 mm. it contains 60.9% of formic acid, the boiling point being 38°. It is therefore possible to obtain concentrated from dilute formic acid by concentrating up to the constant boiling mixture at atmospheric pressure, and then continuing the distillation at low pressure, a separation into very concentrated formic acid and the more dilute constant boiling mixture being obtained.

E. H. R.

Preparation of Anhydrides and Chlorides of Organic Acids.

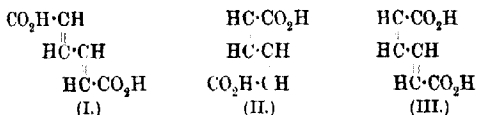
THOMAS HAROLD DURRANS and A. BOAKE, ROBERTS & CO., LTD. (Brit. Pat., 131379; addition to Brit. Pat., 128282).—Organic acid anhydrides or chlorides other than acetic anhydride or chloride may be produced by the action of chlorine on a mixture of phosphorus, preferably red phosphorus, and the alkali or alkaline earth salts of the organic acid, at temperatures preferably below 50°, and in proportions falling within those represented by the following pairs of equations for the anhydrides and chlorides respectively: $6R \cdot CO_2Na + P + 3Cl = 3(R \cdot CO)_2O + Na_3PO_3 + 3NaCl$ and $8R \cdot CO_2Na + P + 5Cl = 4(R \cdot CO)_2O + Na_3PO_3 + 5NaCl$, and $3R \cdot CO_2Na + P + 3Cl = 3R \cdot COCl + Na_3PO_3$ and $4R \cdot CO_2Na + P + 5Cl = 4R \cdot COCl + Na_3PO_4$.

G. F. M.

The Action of Grignard Reagents on the Esters of certain Dicarboxylic Acids. HARRY HEPWORTH (T., 1919, 115, 1203—1210).

Oxidation of Muconic Acid. Synthesis of Mucic Acid.

ROBERT BEHREND and GEORGE HEYER (*Annalen*, 1919, 418, 234—316).—Of the three configurative formulæ possible for muconic acid, formula I is the most probable, since the only tar-



aric acid produced by oxidation with permanganate is *r*-tartaric acid; formic, carbonic, oxalic, mucic, and other unidentified acids are also formed, but the absence of *i*-tartaric acid is definitely ascertained.

Mucic acid is obtained in yields up to 36.5% of the theoretical by oxidising a neutral solution of sodium muconate with sodium chlorate in the presence of a little osmium tetroxide and a few

y*

drops of acetic acid (compare Hofmann, Ehrhart, and Schneider, A., 1913, ii, 609), ridosaccharic acid being also formed in about 2% of the theoretical yield. The latter acid forms a characteristic copper salt, $C_6H_8O_8Cu \cdot 2H_2O$, microscopic prisms which become deep blue by prolonged heating at 120° , and a phenylhydrazide, $C_{18}H_{22}O_8N_4$, faintly yellowish-white, crystalline powder, m. p. $217-218^\circ$ (decomp.). C. S.

Reactions between Potassium Sulphate and Tartaric Acid under Various Conditions. Behaviour of Potassium Hydrogen Sulphate with Alcohol. ARTURO BORNTRAEGER

(*Annali Chim. Appl.*, 1919, 12, 1-23).—The readiness with which the system ($K_2SO_4 + C_4H_6O_6$) is converted into the system ($KHSO_4 + C_4H_5KO_6$) when evaporated with alcohol was shown by Bussy and Buignet (*J. Pharm. Chim.*, 1865, [v], 2, 8). When aqueous solutions containing equivalent quantities of potassium hydrogen sulphate and potassium hydrogen tartrate are evaporated, potassium sulphate and tartaric acid are first formed. On continuing the evaporation, potassium hydrogen tartrate is deposited, and this subsequently reacts with the potassium hydrogen sulphate in solution to form potassium sulphate and tartaric acid. Hence the two systems ($K_2SO_4 + C_4H_6O_6$) and ($KHSO_4 + C_4H_5O_6K$) appears to behave in an identical manner under these conditions. When the evaporation is continued to the end, a dry mixture of potassium sulphate and tartaric acid is obtained, whereas in presence of free sulphuric acid the residue would be moist. Absolutely anhydrous alcohol has no influence on potassium hydrogen sulphate, but alcohol containing a little water decomposes it slowly and partly into the normal sulphate and free sulphuric acid. On treating a dry mixture in equimolecular proportions of potassium sulphate and tartaric acid with ether or absolute alcohol, only the tartaric acid is extracted, but in presence of alcohol containing a little water, a partial reaction takes place, with the formation of potassium hydrogen tartrate and potassium hydrogen sulphate, and the latter is subsequently partly decomposed into the normal sulphate and free sulphuric acid. Similar reactions are observed when solutions of the two substances in equimolecular proportions are evaporated prior to the treatment with ether, absolute alcohol, or alcohol containing a little water. [See also *J. Soc. Chem. Ind.*, 1919, 839a.] C. A. M.

Crystallography of the Compound of Nickel Dichromate and Ethylenediamine, $NiCr_2O_7 \cdot 3C_2H_4(NH_2)_2$. GIUSEPPINA CHIAVARINO (*Riv. min. crist. Ital.*, 1917, 48, 82-85).—This salt is monoclinic; complete crystallographic data are given.

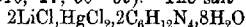
CHEMICAL ABSTRACTS.

Crystallography of the Compounds of Nickel and Magnesium Tetrahydroxide Octahydrates with Hexamethylenetetramine. C. PERRIER (*Riv. min. crist. Ital.*, 1916, 47, 22-30).—The salt of the formula $RS_4O_6 \cdot 2C_6H_{12}N_4 \cdot 8H_2O$,

where R=Mg or Ni, are monoclinic; complete crystallographic data are given. The isomorphism of magnesium and nickel in other compounds is discussed, and the closeness of their molecular volumes is pointed out.

CHEMICAL ABSTRACTS.

Crystallography of Compounds of Lithium Mercuric Haloids with Hexamethylenetetramine. E. QUERCIGH (*Riv. min. crist. Ital.*, 1916, **47**, 30—39).—The salt



is monoclinic, the corresponding bromide triclinic, and the iodide rhombic. Full crystallographic data are given.

CHEMICAL ABSTRACTS.

The Melting Points of the Substituted Amides of the Normal Fatty Acids. PHILIP WILFRED ROBERTSON (T., 1919, 115, 1210—1223).

Action of Alkaline Solutions of Bromine on Acid Amides.

HANS ODENWALD (*Annalen*, 1919, **418**, 316—341).—In the method previously described (Behrend and Odenwald, this vol., i, 70) for the preparation of acetylmethylcarbamide, the yield falls from 75% to zero in the presence of an excess (15—20%) of alkali over the amount (1 mol.) required to react with the acetamide (1 mol.) and bromine (0.55 mol.). The cause of this has now been investigated. In a series of experiments, acetamide (1 mol.) was dissolved in bromine (0.5—2.0 mols.), and the solution was treated with a quantity of 18.7% potassium hydroxide solution (1.2—4.8 mols.) 20% in excess of the amount required to combine with the bromine. Carbon dioxide, ammonia, and methylamine were detected in all experiments; the amounts of these and of unchanged acetamide, in the experiments with less than 1.5 mols. of bromine, account for 0.47—0.49 mol. of acetamide. With 1.5 mols. of bromine, acetylmethylcarbamide (0.078 mol.) was detected, but not acetamide, and in the experiment with 2 mols. of bromine neither acetamide nor acetylmethylcarbamide could be detected, and the amount of carbon dioxide formed corresponded with only 0.3 mol. of acetamide. In all experiments, the balance of the acetamide was converted into products which could not be identified; the products were unsuccessfully examined for the presence of acetonitrile, methyl alcohol, hydrogen cyanide, *N*-dimethylcarbamide, and methylcarbamide, but very small quantities of dibromomethylamine and of nitrogen (about 0.03 mol.) were detected. The author is of opinion that the methylcarbamide in alkaline solution reacts with acetamide either not at all or very much more slowly than in acid solution; instead of forming acetylmethylcarbamide, it decomposes into carbon dioxide and methylamine, and the latter reacts more rapidly than acetamide with the hypobromite.

With the hope of obtaining less volatile products of reaction, the behaviour of an alkaline solution of bromine with *isovaleramide* has been examined. In an experiment with *isovaleramide*

(0.5 mol.), bromine (0.25 mol.), and 10% potassium hydroxide solution (0.6 mol.), the products were carbon dioxide (0.23 mol.), dibromoisobutylamine (0.09 mol.), ammonia and isobutylamine (0.02 mol.); these and unchanged isovaleramide (0.32 mol.) account for the whole of the amide. The reaction proceeds according to the equation $C_4H_9\cdot CO\cdot NH_2 + Br_2 + 2KOH = C_4H_9\cdot NH_2 + CO_2 + 2KBr + H_2O$, but the author has been unable to discover what is the fate of the isobutylamine.

It is possible that a loss of acetamide occurs in the first experiments during the evaporation of solutions. One gram of different amides has been evaporated to dryness with 20 c.c. of water, heated on the water-bath for half an hour, and again evaporated with 20 c.c. of water; the losses were, with acetamide 0.95 gram, with propionamide 0.36 gram, with isobutyramide 0.10 gram, and with isovaleramide nil.

It is quite immaterial in what order acetamide (1 mol.), isovaleramide (1 mol.), bromine (1 mol.), and aqueous potassium hydroxide (2 mols.) are mixed together; the products of the reaction are always the same, namely, about equal quantities (molecular) of isovalerylisobutylcarbamide and acetylisobutylcarbamide, together with a small quantity of acetylmethylcarbamide; it is remarkable that the fourth possible product, isovalerylmethylcarbamide, could not be detected. Analogous results are obtained with acetamide and propionamide, and with acetamide and isobutyramide.

Acetylisobutylcarbamide, $C_7H_{11}O_3N_2$, forms long, six-sided leaflets, m. p. 109–114°, and *acetylisopropylcarbamide*, hexagonal crystals, m. p. 68–72°, which become superficially oily after long keeping. C. S.

The Constitution of Carbamides. X. The Behaviour of Urea and of Thiourea towards Diazomethane and Diazomethane respectively. The Oxidation of Thiourea by Potassium Permanganate. EMIL ALPHONSE WERNER (T, 1919, 115, 1168–1174).

Some Cases of Solubility Influence. I. Compounds of Thiosinnamine [Allylthiocarbamide] Existing in Aqueous Solution. G. BARGELLINI (*Gazzetta*, 1919, 49, i, 175–191).—Cryoscopic investigation of solutions containing thiocarbamide or allylthiocarbamide, together with either sodium salicylate or resorcinol or antipyrine, leads to anomalous results which are explainable on the assumption that compounds between the different pairs of solutes are formed in solution. None of these compounds has been separated in the solid condition. T. H. P.

The Rotatory Powers of the Amides of Several α -Hydroxyacids of the Sugar Group. C. S. HUDSON and SHIGERU KOMATSU (*J. Amer. Chem. Soc.*, 1919, 41, 1141–1147).—The generalisations announced in an earlier paper, based largely on Weerman's work (A., 1918, i, 292), have been amplified and extended by further

and more trustworthy data. The material examined makes it possible to calculate the molecular rotation due to each active carbon atom in a number of series by the method already employed in the case of certain phenylhydrazides (A., 1917, i, 318). The following table gives the values as far as it is possible to determine them, the sign of the rotation being for the isomeride which has the hydroxyl group attached to the particular carbon atom placed to the right of the formula, written vertically, with the amide group at the top.

Carbon.	4-C series diamide.	Pentonic amides.	Hexonic amides.	Heptonic amides.	Hexario diamides.
α	+7880	+4450	+4725	+4585	+3925
β	—	-2315	-1465	-1960	-1385
γ	—	+575	+95	?	—
δ	—	—	-205	-420	—

The values for the β - and γ -carbon atoms in the series of pentonic amides are probably untrustworthy, as they depend on a value of the rotation of *d*-xylonamide which is doubtful.

It is interesting to note how the sign of the rotation alternates from carbon to carbon, and how much the rotation of the whole molecule depends on the configuration about the α - and β -carbon atoms. The table also illustrates the principle of optical superposition in the sugar group.

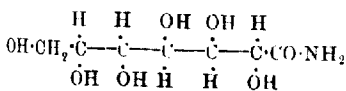
The amides prepared by the authors themselves, usually by the action of ammonia on the lactones, are as follows, the values of $[\alpha]_D^{20}$ being for aqueous solutions: *d*-galactonamide, m. p. 172—172.5°, $[\alpha]_D^{20} + 30.2^\circ$; *d*-gluconamide, m. p. 143—144°, $[\alpha]_D^{20} + 31.2^\circ$; *d*-gulonamide, m. p. 122—123°, $[\alpha]_D^{20} + 15.2^\circ$; *d*-mannonamide, m. p. 172—173°, $[\alpha]_D^{20} - 17.3^\circ$; α -*d*-glucoheptonamide, m. p. 134.5°, $[\alpha]_D^{20} + 10.6^\circ$; β -*d*-glucoheptonamide, m. p. 158°, $[\alpha]_D^{20} - 30.2^\circ$; α -*d*-galactoheptonamide, m. p. 206°, $[\alpha]_D^{20} + 14.3^\circ$; *l*-arabonamide, m. p. 135—136°, $[\alpha]_D^{20} + 37.5^\circ$; *l*-ribonamide, m. p. 137—138°, $[\alpha]_D^{20} - 16.4^\circ$; *d*-mannosaccharodiamide, m. p. 188—189.5° (decomp.), $[\alpha]_D^{20} - 24.5^\circ$; *d*-saccharodiamide, m. p. 172—173°, $[\alpha]_D^{20} + 13.3^\circ$.

J. C. W.

The Amide of α -*d*-Mannoheptonic Acid. C. S. HUDSON and K. P. MONROE (*J. Amer. Chem. Soc.*, 1919, **41**, 1140—1141).—This amide was first obtained by Fischer by the action of hydrogen cyanide on *d*-mannose, but it is not easy to purify it if made in this way. A better method is the action of ammonia on a solution of α -*d*-mannoheptonolactone in 50% alcohol. α -*d*-Mannoheptanamide (annexed

formula) has m. p. 193—194° and $[\alpha]_D^{20} + 28.0^\circ$, the molecular rotation being almost the same as that of *d*-galactonamide and *l*-arabonamide, in which the configuration of the molecule with regard to the α -, β -, and γ -carbon atoms is the same.

J. C. W.



Preparation of Cyanogen Chloride. W. L. JENNINGS and W. B. SCOTT (*J. Amer. Chem. Soc.*, 1919, 41, 1241—1248).—The authors review the history of cyanogen chloride, and report that the most suitable reaction for its preparation is that of chlorine on an alkali cyanide. Water is necessary in this reaction, but its amount must be restricted, otherwise too much heat is developed and some of the product is polymerised. The best procedure is as follows. Finely powdered sodium cyanide is mixed with 2% of its weight of water and just sufficient carbon tetrachloride to prevent the mass from becoming pasty. The mixture is cooled to -5° and submitted to the action of a current of well-washed chlorine, so regulated that the temperature is maintained at about -3° . The flask is connected with a calcium chloride tube and then a U-tube immersed in a freezing mixture, and when absorption is complete, as indicated by a bubbler at the final exit, the temperature is allowed to rise to 10° , and finally to 23° , so as to distil the cyanogen chloride. The crude product is usually of a yellow colour through dissolved chlorine, but this is removed by freezing or by leaving the liquid over mercury in a sealed tube. The yield is almost quantitative, and there are no risks of explosion.

Pure cyanogen chloride is a colourless liquid, b. p. $13^{\circ}/748$ mm., m. p. -5° to -6° , and does not polymerise. The presence of traces of hydrogen chloride, however, induces polymerisation, and if suspected should be counteracted by treatment with lime.

J. C. W.

Preparation of Cyanogen Chloride by Held's Method. CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1919, 169, 383—386).—Held's method for preparing cyanogen chloride from potassium cyanide and chlorine (A., 1898, i, 547) gives good results only if the proportion of zinc sulphate added is that required by the equation $4\text{KCN} + \text{ZnSO}_4 = \text{Zn}(\text{CN})_2 + 2\text{KCN} + \text{K}_2\text{SO}_4$, a yield of 80% being then obtained. Methods for controlling the purity of the product are described.

T. H. P.

Compounds of Univalent Nickel. II. I. BELLUCCI (*Gazzetta*, 1919, 49, ii, 70—81. Compare A., 1914, i, 260; also Tschugaev and Chlopov, A., 1914, ii, 660).—The aqueous solution of red potassium nickelocyanide, $\text{K}_2\text{Ni}(\text{CN})_3$, prepared by gradual addition of alkali metal amalgam to the aqueous solution of the yellow nickelocyanide, $\text{K}_2\text{Ni}(\text{CN})_4$, in an atmosphere of hydrogen, readily assumes the original yellow colour, oxidation being effected either by atmospheric oxygen, or by aqueous oxygen with liberation of the hydrogen, or by an oxidising agent such as hydrogen peroxide. The red solution may be preserved from appreciable oxidation for some days by employing boiled water in its preparation and by adding concentrated potassium hydroxide solution to the liquid and covering the latter with a layer of light petroleum.

Oxidation of the red nickelocyanide by means of hydrogen peroxide in absence of alkali cyanide takes place according to the

equation, $4\text{K}_2\text{Ni}(\text{CN})_3 + 2\text{H}_2\text{O}_2 = 3\text{K}_2\text{Ni}(\text{CN})_4 + \text{Ni}(\text{OH})_2 + 2\text{KOH}$. Further, when an aqueous solution of the pure, red nickelocyanide is boiled for some time in a reflux apparatus in a stream of hydrogen, metallic nickel is precipitated, and the yellow nickelocyanide remains in the solution, the proportions of the total nickel in precipitate and solution being very nearly 1:3 (actually 1:3.16): $4\text{K}_2\text{Ni}(\text{CN})_3 + 2\text{H}_2\text{O} = 3\text{K}_2\text{Ni}(\text{CN})_4 + \text{Ni} + 2\text{KOH} + \text{H}_2$; the same reaction occurs, only far more slowly, at the ordinary temperature. Such separation of metallic nickel from a compound of univalent nickel may be represented by the scheme, $2\text{Ni}' \rightarrow \text{Ni}'' + \text{Ni}$, and is analogous to the separation of copper from a cuprous salt with formation of a cupric salt, $2\text{Cu}' \rightarrow \text{Cu}'' + \text{Cu}$.

T. H. P.

Production of Aromatic Nitro-compounds. FERDINAND GROS & BOUCHARDY and LUCIEN JEAN JOSEPH PERRUCHE (Brit. Pat., 131982).—Aromatic nitro-compounds are prepared by passing oxygen, air, or ozonised air, preferably under pressure, into a mixture of the substance to be nitrated with liquid nitrogen peroxide and traces of water, the temperature being maintained at 0–20°. Nitric acid is first produced according to the equation $\text{N}_2\text{O}_4 + \text{H}_2\text{O} + \text{O} = 2\text{HNO}_3$, and instantly reacts with the aromatic compound, regenerating water, and the cycle of operations is repeated until the reaction mixture contains only the nitro-compound, nitric acid, and the excess of nitrogen peroxide used; the last is recovered by distillation or by a current of hot air. The nitro-compound may then be isolated after neutralising the nitric acid, or it may be further nitrated by treating the residual mixture with sulphuric acid. If necessary, the violence of the nitration may be moderated by adding to the reaction mixture an inert diluent, such as carbon tetrachloride, before admitting the oxygen.

G. F. M.

Preparation of N-Monoalkyl Derivatives of certain Aromatic Compounds. ARTHUR LAPWORTH and LEVINSTEIN, LTD. (Eng. Pat., 132555).—Benzylidene derivatives of *p*-substituted monoamines or of other monoamines of the benzene and naphthalene series substituted by indifferent groups in the nucleus, which either as amines or as alkylamines do not react with benzaldehyde in the presence of acids to form amino-derivatives of triarylmethanes, are treated in the absence of alkali with alkyl sulphates or alkyl esters of benzenesulphonic acid. The products are hydrolysed and the *N*-monoalkylarylamines are separated from the mixture. Examples of the process are described in relation to the benzylidene derivatives of *p*-aminophenol, *p*-toluidine, and 1-bromo-2-naphthylamine. The benzylidene compound is dissolved in boiling benzene, the pure alkylating agent, such as methyl sulphate, is added, and the mixture boiled for some hours. The product is hydrolysed by the addition of hydrochloric acid and a little water, the benzaldehyde and benzene are removed by distillation with steam, the *N*-alkylated base is liberated from the residue and

separated from the other products in any suitable manner, for example, by conversion into the nitroso-compound. J. F. B.

Preparation of Diphenylamine. HOMER ROGERS and E. J. DU PONT DE NEMOURS & Co. (U.S. Pat. 1314538).—The condensation of aniline to diphenylamine is effected by heating the aniline in the presence of water and a catalyst consisting of a substance containing bromine. J. F. B.

β -Naphthylmethylamine. GILBERT T. MORGAN and FREDERICK PAGE EVANS (T., 1919, 115, 1140—1145).

The Oxidation of Phenol Derivatives. CYRIL NORMAN HINSHELWOOD (T., 1919, 115, 1180—1188).

Oxidation of Phenols by Gaseous Oxygen and the Catalytic Effect of Metals. F. W. SKIRROW (*Canadian Chem. J.*, 1919, 3, 292—294).—The oxidation which takes place when *o*-cresol or a solution of cresol in benzene is brought into contact with air or oxygen in the presence of copper was measured by connecting the tube containing the reacting substances with a mercury manometer and recording the rate of absorption by the fall in pressure. It was found that there was an initial period during which there was little, if any, absorption. In a blank experiment in which the air in the tube was replaced by nitrogen, no absorption occurred, and the cresol in the tube did not darken even after three years' exposure to light. In another series of experiments, the flask containing the benzene solution of cresol and the copper was connected with a gas burette containing oxygen saturated with benzene over mercury, and the decrease in the volume was measured in the usual way. Here, too, the initial delay in the absorption was noticed, and this was attributed either to the presence of a substance retarding the oxidation or to the necessity of the formation of a catalytic compound. In support of the former view was the fact that the oxidation proceeded more consistently when the oxygen derived from potassium chlorate was replaced by electrolytic oxygen freed from all traces of ozone. Green crystals containing 44.9% of copper (after drying at 100°) were present in the dark liquid after the oxidation. As this amount of copper does not correspond with the composition of any of the probable compounds, it is possible that the benzene ring is broken during the absorption. A similar oxidation was observed in the case of phenol, but more slowly than with *o*-cresol, and here too the initial stage of very slow absorption was present. [See also *J. Soc. Chem. Ind.*, 1919, 812A.] C. A. M.

Chloropicrin. I. JOHN ADDYMAN GARDNER and FRANCIS WILLIAM FOX (T., 1919, 115, 1188—1194).

Crystallography of Ammonium Picrate and of Potassium Trithionate. HERBERT E. MERWIN (*J. Washington Acad. Sci.*, 1919, 9, 429—431).—The orthorhombic crystals of ammonium

picrate are tabular, acicular, or granular in habit. Optical constants are given; refractive indices (Na) $\alpha=1.508$, $\beta=1.872$, $\gamma=1.908$. There is a change in the optic axial plane for different colours, and at wave-length 541μ the crystals are optically uniaxial. Blades of potassium trithionate crystallised from a hot saturated solution show a slight variation in the angles of the prism. Optical constants are given; refractive indices (Na) $\alpha=1.4934$, $\beta=1.5641$, $\gamma=1.602$.
L. J. S.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. VII. Chain Compounds of Sulphur (*continued*).
SIR PRAFULA CHANDRA RAY and PRAFULA CHANDRA GUHA (T., 1919, 115, 1148—1155).

The Electrolytic Reduction of Phenylacetic Acid. C. MARIE, R. MARQUIS, and BIRCKENSTOCK (*Bull. Soc. chim.*, 1919, [iv], 25, 512—516).—Phenylacetic acid can be reduced by electrolytic methods in a sulphuric acid solution, using a lead cathode. The yield is small, owing to a portion of the phenylethyl alcohol formed combining with the sulphuric acid and being subsequently oxidised at the anode. The only portion of the alcohol which escapes this destruction is that which, at the moment of its formation, combines with the excess of phenylacetic acid present. W. G.

Syntheses of Naphthyl-lactic and Naphthylcinnamic Acids.

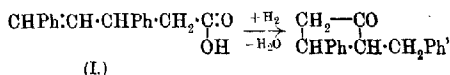
I. β -Phenyl- β - α -naphthyl-lactic Acid and β - α -Naphthylcinnamic Acid. REMO DE FAZI (*Gazzetta*, 1919, 49, i, 242—251).— β -Phenyl- β - α -naphthyl-lactic acid, $C_{10}H_7\cdot CPh(OH)\cdot CH_2\cdot CO_2H$, obtained as ethyl ester by decomposing by means of acidified water, the complex, $C_{10}H_7\cdot CPh(O\cdot ZnBr)\cdot CH_2\cdot CO_2Et$, formed by the interaction of phenyl α -naphthyl ketone and ethyl bromoacetate in presence of zinc dust, crystallises in slender, colourless, silky needles of peculiar odour, m. p. 188—189°, and with concentrated sulphuric acid in the cold gives a transitory, green coloration changing to reddish-brown. Its ethyl ester forms tufts of slender, white needles, m. p. 95—96°, and gives the same colorations with sulphuric acid as the free acid.

β - α -Naphthylcinnamic acid, $C_{10}H_7\cdot CPh\cdot CH\cdot CO_2H$, obtained as ethyl ester by dehydrating ethyl β -phenyl- β - α -naphthyl-lactate in benzene solution by means of phosphoric oxide, forms silky, white needles, m. p. 219—220°. With concentrated sulphuric acid it first gives a transitory, emerald-green coloration, and then dissolves to a reddish-brown solution with a green fluorescence; on addition of water, the acid solution becomes yellow and yields a precipitate, which is probably the corresponding indone. The ethyl ester forms a pale yellow oil, b. p. 278—281°/2 mm., or shining needles, m. p. 69—71° (?), and with concentrated sulphuric acid gives a transitory, green coloration, rapidly changing to reddish-brown.

T. H. P.

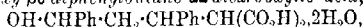
Asymmetric Replacement in the meta-Series. I. WILLIAM HENRY GOUGH and JOCELYN FIELD THORPE (T., 1919, 115, 1155—1164).

Some Factors bearing on 1:6-Addition. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1919, **41**, 1132—1140).—In all the cases in which addition in the 1:6-position has been observed, the unsaturated compound has also had an ethylenic linking in the 3:4-position (compare Straus, A., 1910, i, 119). The author has now synthesised the compound (I) without this disturbing element, but finds that it is abnormal in behaviour. When reduced, for example, it was expected to yield a ketone, thus:



but it could not be reduced either by zinc and acetic acid or sodium amalgam.

Phenyl styryl ketone is condensed with methyl or ethyl malonate (Kohler, A., 1911, i, 984), the esters are hydrolysed, and the ketonic acid is reduced by means of sodium amalgam. Two by-products of the reduction are mentioned, namely, *βδ*-diphenylvalerolactone, $\text{O} \begin{matrix} \text{CHPh}\cdot\text{CH}_2 \\ \text{CO---CH}_2 \end{matrix} \text{CHPh}$, needles, m. p. 113—114°, and *δ*-hydroxy-*βδ*-diphenylbutane-*αα*-dicarboxylic acid,



nodules of stout needles, m. p. 190—195° (decomp.), but the chief product is *δ*-hydroxy-*βδ*-diphenylvaleric acid, which crystallises with 0.5H₂O. in needles from benzene or pearly flakes from alcohol, m. p. 154—154.5°. When boiled with acetic anhydride and a little sulphuric acid, this compound changes into the desired unsaturated acid, accompanied in one experiment by an internal ester, $\text{O} \begin{matrix} \text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO} \\ \text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh} \end{matrix} \text{O}$, m. p. 92—94°.

βδ-Diphenyl-*Δ*-butene-*α*-carboxylic acid (I) crystallises from benzene in colourless, rhombic needles, m. p. 124—125°, and forms a methyl ester, clusters of stout needles, m. p. 47—48°, which reacts with magnesium phenyl bromide to form the carbinol, CHPh:CH·CHPh·CH₂·CPh₂·OH, in thin needles, m. p. 138—139°.

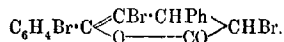
J. C. W.

The cycloPropane Series. V. E. P. KOHLER and L. L. STEELE (*J. Amer. Chem. Soc.*, 1919, **41**, 1093—1105. Compare A., 1917, i, 566—570; 1918, i, 72; this vol., i, 404).—All the cyclopropane derivatives described in the earlier papers have had two carboxyl groups (or ester groups) attached to one of the ring carbon atoms. The authors have now attempted to prepare monocarboxylic acids of this series, but have encountered great difficulties before achieving a measure of success.

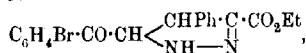
In the first place, benzoylphenylcyclopropanedicarboxylic acid loses carbon dioxide on heating, but the yield of the monocarboxylic acid is insignificant, no matter what modifications of the treatment are tried (compare A., 1917, i, 566).

A second scheme is based on the elimination of hydrogen bromide

from an α -bromo-ketonic ester. γ -p-Bromobenzoyl- β -phenylbutyric acid, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, needles, m. p. 152—153°, is prepared by heating the corresponding malonic acid (A., 1918, i, 72), converted into the methyl ester, stout needles, m. p. 93°, and this is brominated. Methyl γ -bromo- γ -p-bromobenzoyl- β -phenylbutyrate is obtained in two forms, chiefly slender needles, m. p. 81—82°, but also long, feathery crystals, m. p. 92°. When it is heated with potassium acetate in methyl alcohol, the product is not a cyclopropane derivative, but γ -p-bromobenzoyl- β -phenylbutyrolactone, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}\begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix}\text{CO} \\ \diagdown \text{CHPh}\cdot\text{CH}_2$, colourless needles, m. p. 158°. The same lactone may be obtained by the action of sodium carbonate on γ -bromo- γ -p-bromobenzoyl- β -phenylbutyric acid, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. 146—147°, this being formed by the bromination of the above free butyric acid derivative. In addition, when this γ -bromo-acid is warmed with phosphorus tribromide and bromine, it yields a compound which crystallises in large, rhombic crystals, like smoky quartz, and is probably represented by the formula



The successful scheme is an adaptation of Buchner's method for preparing cyclopropane acids from pyrazolines. $\alpha\beta$ -Unsaturated ketones are condensed with ethyl diazoacetate to give ketonic pyrazolines, and these are heated. The chief product is a pyrone, but a yield of about 40% of a cyclopropane derivative may be obtained if the decomposition is carried out in the presence of platinum scrap. In the preliminary trials of this scheme, β -bromophenyl styryl ketone was used. When heated with ethyl diazoacetate at 95—175°, this yields an ester which may be hydrolysed to 5-p-bromobenzoyl-4-phenylpyrazole-3-carboxylic acid, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{C}\begin{smallmatrix} \text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{H} \\ \diagup \text{NH-N} \end{smallmatrix}$, feathery needles, m. p. 216—217° (decomp.), which changes at 245° into 5-p-bromobenzoyl-4-phenylpyrazole, m. p. 159°. If the reaction mixture is diluted with light petroleum, however, the product is the desired ethyl 5-p-bromobenzoyl-4-phenylpyrazole-3-carboxylate,



rhombic plates, m. p. 150—154° (decomp.). This loses nitrogen at 170—200°, changing into a mixture of 6-p-bromophenyl-4-phenyl-1:2-pyrone, feathery crystals, m. p. 183°, and a trace of ethyl 3-p-bromophenyl-2-phenylcyclopropane-1-carboxylate, needles, m. p. 118—119°.

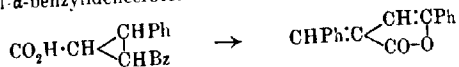


In the main experiments, unsubstituted phenyl styryl ketone was

used. This reacts with ethyl diazoacetate as above to form *ethyl 5-benzoyl-4-phenylpyrazoline-3-carboxylate*. This crystallises in hexagonal plates, m. p. 156—158°, which change when kept for some time just below the decomposition temperature into an *isomeride*, needles, m. p. 102·5—103°. Both forms, in alcoholic solution, give a vivid red colour with a trace of hydrogen chloride. When heated alone at a high temperature, the product consists almost entirely of 4:6-diphenyl-1:2-pyrone, yellow plates, m. p. 138—139°, but in the presence of platinum, at 220—225°, a 37% yield of *ethyl 3-benzoyl-2-phenylcyclopropane-1-carboxylate* is obtained. This crystallises in thin plates, m. p. 103°, is stable at 300°, and does not reduce an acetone solution of permanganate.

The free acid, $\text{CO}_2\text{H}\cdot\text{CH}\begin{smallmatrix} \text{CHPh} \\ \text{CHBz} \end{smallmatrix}$, as obtained by hydrolysis with aqueous-alcoholic potassium hydroxide in the cold, exists in two stereoisomeric forms, slender needles, m. p. 176°, and long threads, m. p. 147—150°, the latter being the more soluble in benzene, and yielding an isomeric *ethyl ester*, m. p. 93—94°, when its silver salt is treated with ethyl iodide.

It is interesting to compare the new acid and ester with Buchner's 2-phenylcyclopropane-1:3-dicarboxylic acid and the 3-benzoyl-2-phenylcyclopropane-1:1-dicarboxylic acid of the earlier papers. The new acid is decomposed when heated with hydrobromic acid in a sealed tube, whereas Buchner's acid is quite stable. When left with hydrogen bromide dissolved in acetic acid, however, it suffers rupture of the ring between carbon atoms 2 and 3, like the 1:1-dicarboxylic acid, only more readily, the product being γ -phenyl- α -benzylidenecrotonolactone, thus:



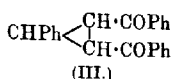
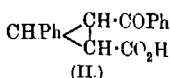
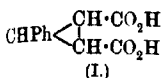
(see A., 1917, i, 566). Hydrochloric acid under the same conditions gives an unstable *acid*, $\text{CHPhCl}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\text{Bz}$, m. p. 131—132°, which changes above its m. p. into β -benzylidenepropiophenone, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Bz}$. The corresponding ester, *ethyl β -chloro- α -phenacyl- β -phenylpropionate*, hexagonal plates, m. p. 68—69°, is stable, and may be obtained most readily by the action of alcoholic hydrogen chloride on the cyclic acid or its ester. The cyclic ester also behaves as an unsaturated compound towards zinc and acetic acid, being reduced to the ester of γ -benzoyl- β -phenylpropionic acid. A great difference between methyl 3-benzoyl-2-phenylcyclopropane-1-carboxylate and the 1:1-dicarboxylates, however, lies in their behaviour towards basic agents. The latter are most easily ruptured between the carbon atoms 1 and 3, but the new ester is indifferent to dry alkyl oxides, and no means of effecting the same opening of the ring have been found.

ω -Nitrostyrene also reacts very vigorously with ethyl diazoacetate, but the primary nitropyrazoline loses nitrous acid so readily that it changes spontaneously into *ethyl 4-phenylpyrazoline-3-carboxylate*, plates, m. p. 164—165°. The corresponding *acid*,

$\text{CO}_2\text{H}\cdot\text{C} \begin{smallmatrix} \text{CPh}\cdot\text{CH} \\ \text{N}\text{---}\text{NH} \end{smallmatrix}$ m. p. 252–253°, changes into 4-phenylpyrazole when heated above 250°.

J. C. W.

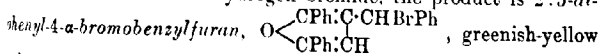
The cycloPropane Series. VI. E. P. KOHLER and W. N. JONES (*J. Amer. Chem. Soc.*, 1919, **41**, 1249–1263).—In the last paper (preceding abstract) a comparison was made between the properties of the cyclopropanedicarboxylic acid (I) and the ketonic acid (II). The diketone (III) has now been synthesised and studied in the same manner.



Benzylidenediacetophenone (Kostanecki, A., 1896, i, 556) reacts with bromine in slightly warmed chloroform to give two products, according to the proportion of bromine, namely, β -bromo- α -*tri*-phenylpentane- α -dione, $\text{COPh}\cdot\text{CHBr}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh}$, m. p. 131° (decomp.), and $\beta\beta$ -dibromo- α -*tri*-phenylpentane- α -dione, m. p. 149° (decomp.). Both substances may be converted into 1:2-dibenzoyl-3-phenylcyclopropane, the former by treatment with sodium ethoxide solution, giving a modification which crystallises in needles, m. p. 116°, the latter by boiling with alcoholic potassium iodide, giving an isomeride which has m. p. 151°, but changes into the form with m. p. 116° on crystallisation from alcohol containing 1% of sodium hydroxide. Both forms of the diketone yield the same *monoxime*, m. p. 144°, and *dioxime*, needles, m. p. 175°.

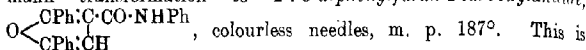
The diketone is remarkably sensitive to reducing agents. When boiled with moist alcohol and zinc dust, it forms the parent benzylidenediacetophenone, the ring being opened at the point where it was originally closed.

Unlike the ketonic acid (II), the diketone does not react with alcoholic solutions of hydrogen chloride or bromide. With glacial acetic acid solutions, however, it behaves like other cyclopropane derivatives described in this series of papers, the ring being opened between the carbon atoms 2 and 3. The resulting 1:4-diketone then loses water and changes, as usual, into a furan derivative. Thus, with a solution of hydrogen bromide, the product is 2:5-di-



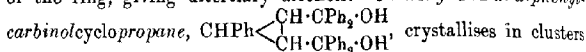
prisms, m. p. 110°. This is capable of yielding a number of reactive substances, through which it may ultimately be converted into 2:5-diphenylfuran, and thus identified. With potassium acetate and acetic acid, for example, it forms 2:5-diphenyl-4-acetoxylbenzylfuran, yellow needles, m. p. 84°, which may be hydrolysed by alcoholic hydrochloric acid to 2:5-diphenyl-4- α -hydroxybenzylfuran. This may also be obtained by the action of sodium methoxide solution on the bromobenzyl compound. It

crystallises in needles, m. p. 105°, and may be oxidised by chromic acid in cold acetic acid solution to a *product*, $C_{22}H_{18}O_3 \cdot H_2O$, m. p. 89°, which readily loses $1H_2O$ at 110°, or $2H_2O$ when boiled with alcoholic potassium hydroxide, methyl-alcoholic hydrogen chloride, or acetic anhydride and sodium acetate, giving 4-benzoyl-2:5-diphenylfuran, which crystallises in yellow needles, and forms a 3-bromo-compound, m. p. 120°, when treated with bromine in chloroform. The *oxime* of the benzoyl derivative crystallises in rosettes of needles, m. p. 174°, and readily undergoes the Beckmann transformation to 2:5-diphenylfuran-4-carboxylanilide,



hydrolysed by alcoholic potassium hydroxide to the known 2:5-diphenylfuran-4-carboxylic acid, m. p. 217°, which changes into 2:5-diphenylfuran when distilled with zinc dust.

The cyclic diketone reacts with Grignard agents without rupture of the ring, giving ditertiary alcohols. 3-Phenyl-1:2-di-diphenyl-



of slender needles, m. p. 183°, and 3-phenyl-1:2-di- α -phenyl- α -ethyl-carbinolcyclopropane has m. p. 129°.

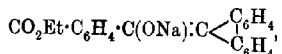
The diketone reacts with phosphorus pentachloride in boiling benzene to form $\alpha\delta$ -dichloro- γ -benzoyl- $\alpha\delta$ -diphenyl- Δ^2 -butene, $\text{CHPhCl} \cdot \text{CHBz} \cdot \text{CH} \cdot \text{CPhCl}$, m. p. 122°, which is transformed into α -chloro- γ -benzoyl- $\alpha\delta$ -diphenyl- Δ^2 -butadiene, prisms, m. p. 84°, when boiled with methyl-alcoholic potassium acetate. The latter compound reacts with magnesium phenyl chloride to give α -chloro- γ -benzoyl- $\alpha\delta\delta$ -triphenyl- Δ^2 -butene, $\text{CHPh}_2 \cdot \text{CHBz} \cdot \text{CH} \cdot \text{CPhCl}$, in large, colourless prisms, m. p. 140°.

The action of bromine in warm chloroform on the cyclic diketone is somewhat obscure, but the *product*, $C_{22}H_{18}O_2 \cdot Br_2$, m. p. 129° (decomp.), is isomeric with the dibromide obtained in the first instance from benzyldenediacetophenone, since it yields the same compounds when treated with potassium iodide or alcoholic potassium acetate. In the latter reaction, the product is either 2-bromo-1:2-dibenzoyl-3-phenylcyclopropane, needles, m. p. 122°, or 2-acetoxy-1:2-dibenzoyl-3-phenylcyclopropane, m. p. 159°, according to the proportion of potassium acetate employed. The latter could not be hydrolysed to the hydroxy-derivative. Alkaline agents give oily residues, whilst treatment with alcoholic hydrogen chloride results in the formation of 2-benzoyl-3:5-diphenylfuran, which crystallises in plates, m. p. 118°, forms a 4-bromo-derivative, m. p. 110°, and may be reduced by means of zinc and acetic acid to 3:5-diphenyl-2-benzylfuran, bright yellow needles, m. p. 193°. The *oxime* of the benzoyl compound, m. p. 152°, suffers the Beckmann transformation to 3:5-diphenylfuran-2-carboxylanilide, $\begin{array}{l} \text{CH} \cdot \text{CPh} \cdot \text{O} \\ \text{CHPh} = \text{C} \cdot \text{CO} \cdot \text{NHPH} \end{array}$, m. p. 143°, and this may be hydrolysed to 3:5-diphenylfuran-2-carboxylic acid, m. p. 194°

(decomp.). This acid yields the known 3:5-diphenylfuran when distilled with zinc dust (Engler and Dengler, A., 1893, i, 512).

J. C. W.

Condensation of Ethyl Phthalate with Fluorene. WILHELM WISLICENUS and PETER NEBER (*Annalen*, 1919, **418**, 274—293).—A mixture of fluorene (1 mol.), sodium (1 atom), and ethyl phthalate (about 1.14 mols.) is heated on the water-bath until the sodium has disappeared, and is then treated, after cooling, with benzene and ice, whereby the sodium derivative of ethyl fluorene-phthaloylate (*o*-carbethoxyphenyl fluorenyl ketone),

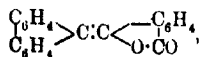


yellowish-white needles with $5\text{H}_2\text{O}$, is obtained, which is remarkably stable to boiling dilute alkali hydroxide solution. In aqueous solution it is decomposed by carbon dioxide or dilute hydrochloric

acid, yielding the α -modification, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{C}\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, of *o*-carbethoxyphenyl fluorenyl ketone, microscopic prisms, m. p. 217—218°; lower m. p.'s, dependent on the method of crystallisation, are frequently obtained in consequence of partial conversion into the β -modification. The α -modification does not react with ferric chloride, but it decolorises bromine in alcoholic solution and forms a copper derivative, $(\text{C}_{23}\text{H}_{17}\text{O}_3)_2\text{Cu}\cdot\text{H}_2\text{O}$, bluish-green needles, m. p. about 180°; by bromination in chloroform in the presence of a little phosphorus pentabromide, it yields *o*-carbethoxyphenyl 3-bromofluorenyl ketone, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CBr}\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, colourless prisms, m. p. 190—191°.

By keeping for several weeks, the α -modification changes into the stable β -modification, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, colourless leaflets or prisms, m. p. 140—141°. The change is effected more rapidly by distillation in a vacuum, by heating at 220°, or, most simply, by boiling with alcohol. The conversion of the β - into the α -modification is effected, through the sodium derivative, by means of alcoholic sodium hydroxide solution. The β -modification does not form a copper derivative and does not react with bromine in alcoholic solution. Both modifications are remarkably stable to alkalis; they are only decomposed by an excess of alcoholic alkali at 150°, yielding ethyl alcohol, alkali phthalate, and fluorene.

By heating above 220°, by distillation in a vacuum or, best, by heating with potassium hydrogen sulphate at 230°, either modification is converted into *phthalylfluorene*, yellow, flattened needles, m. p. 204—206°. To this substance is ascribed, not the indanedi-one formula, but the asymmetric constitution,

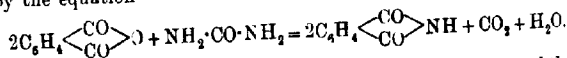


in order to account for its intense yellow colour, its easy decomposition by alkalis into *fluorenephthaloylic acid* (*o*-carboxyphenyl *fluorenyl ketone*), $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}<\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, colourless crystals, m. p. 188—189° (yellow *dipotassium salt*, $\text{C}_{21}\text{H}_{12}\text{O}_3\text{K}_2$), and its conversion in boiling alcoholic solution by an excess of hydrazine hydrate into fluorene and phthalylhydrazide. It can also be prepared by heating a mixture of phthalic anhydride, fluorene, and anhydrous potassium acetate at 200—220°.

The *hydrazide*, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}<\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$, glassy plates, prepared by shaking a suspension of phthalylfluorene in alcohol with hydrazine hydrate, does not melt below 200° when examined in the usual manner, but melts with decomposition (loss of water) when placed in a bath heated at 190°, and then resolidifies. When heated for half an hour at 220°, it is converted into 1-*fluorenyl-phthalazone*, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}>\text{CH}\cdot\text{C}<\begin{smallmatrix} \text{N} \\ \text{C}_6\text{H}_4 \end{smallmatrix}\text{---NH}$, leaflets, m. p. 275—277°.

Phthalylfluorene is reduced to *o*-fluorenylmethylbenzoic acid, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}>\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, groups of faintly yellow needles, m. p. 185—186°, by heating with fuming hydriodic acid and amorphous phosphorus at 160° for eight hours. C. S.

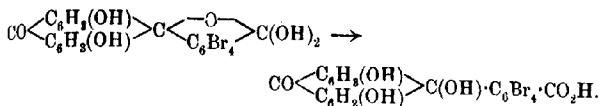
Method for the Preparation of Phthalimide. WALTER HERZOG (*Zeitsch. angew. Chem.*, 1919, **32**, 301).—Phthalic anhydride (2 mols.) and carbamide (1 mol.) are heated together in a long-necked flask; reaction commences at 130° to 135°, and the temperature rises to 150° without further external heating. At the end of the reaction, the liquid mass solidifies suddenly. When cold, the porous solid is washed with a small quantity of water and dried; it consists of practically pure phthalimide m. p. 230—231°, the yield being 90% or more of the amount required by the equation



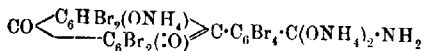
A similar reaction takes place between thiocarbamide and phthalic anhydride, but not between carbamide and succinic anhydride, citraconic anhydride, or camphoric anhydride. W. P. S.

Phthalic Acid Derivatives; Constitution and Colour.
XVII. Tetrabromofluorescein, Tetrabromoeosin, and some of their Derivatives. DAVID S. PRATT, G. F. HUTCHINSON, and A. W. HARVEY (*J. Amer. Chem. Soc.*, 1919, **41**, 1293—1297).—Compare the analogous iodine compounds, A., 1918, i, 175. Tetrabromofluorescein, $\text{C}_{20}\text{H}_2\text{O}_5\text{Br}_4$, dissolves in alkali hydroxides with about the same colour as fluorescein, and is precipitated as a yellow hydrate on the addition of an acid. When this is dried in

a steam-oven, the brick-red, quinonoid form of tetrabromofluorescein is left, but this changes into the yellow, benzenoid form when wetted with acetone or ethyl acetate. The hydrate changes into the very pale yellow *tetrabromofluoresceincarbinolcarboxylic acid* when treated with alcohol, thus:



Anhydrous tetrabromofluorescein forms a bright red *diammonium* salt and a colourless *diacetate*, and reacts with bromine to give *tetrabromofluorescein* (tetrabromoeosin). This is almost colourless, but so sensitive to alkalis that it is generally faintly pink. It dyes silk an attractive pink shade, and forms a *diacetate*, crystallising with $1\text{C}_6\text{H}_6$, and a *tetra-ammonium* salt, of a brilliant, deep bronze colour, probably represented by the formula



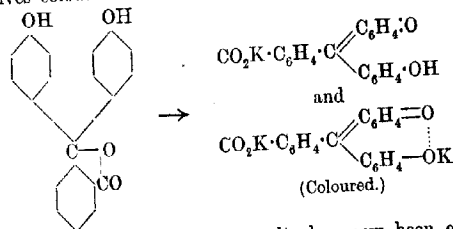
J. C. W.

Phthalic Acid Derivatives; Constitution and Colour.
XVI. Phenoltetrabromophthalein and some of its Derivatives. DAVID S. PRATT, F. B. DOANE, and A. W. HARVEY (*J. Amer. Chem. Soc.*, 1919, **41**, 1289—1293. Compare A., 1918, i. 167—172, 175—177, 540—541).—Tetrabromophthalic anhydride (*ibid.*, 540) condenses with phenol in the presence of fuming sulphuric acid (15% SO_3) to form *tetrabromofluoran*, $\text{C}_{20}\text{H}_5\text{O}_3\text{Br}_4$, colourless crystals, insoluble in alcohol, and a 75% yield of *phenoltetrabromophthalein*, $\text{C}_{20}\text{H}_{10}\text{O}_4\text{Br}_4$, which is nearly white, gives colourless solutions in most solvents, is indifferent to ammonia, but very sensitive to alkali hydroxides. The phthalein yields a colourless, crystalline *diacetate*, *dibenzoate*, and *dimethyl ether*, and may be brominated in boiling alcohol. *Tetrabromophenoltetrabromophthalein*, $\text{C}_{20}\text{H}_6\text{O}_4\text{Br}_8$, forms very pale yellow crystals, dissolves in alkali hydroxides with a brilliant blue colour, reacts with ammonia gas to give a turquoise-blue *diammonium* salt, and yields a colourless *diacetate* and *dibenzoate*, which both crystallise with one molecular proportion of benzene.

J. C. W.

The Quinone-Phenolate Theory of Indicators. The Reactions of Phenolsulphonphthalein and its Bromo- and Nitro-derivatives, and their Monobasic and Dibasic Salts. E. C. WHITE and S. F. ACREE (*J. Amer. Chem. Soc.*, 1919, **41**, 1190—1212. Compare A., 1918, ii. 328; this vol., ii. 400).—In the theory of indicators developed by Acree, it is held that the production of colour in the case of phenolphthalein does not begin when the lactone ring is opened, but when quinone-phenolate ions

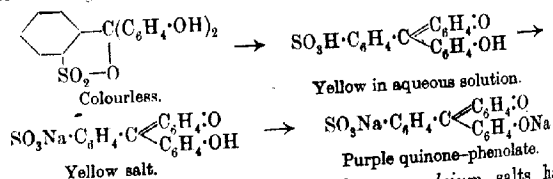
are formed. That is, phenolphthalein is regarded as a substance which gives colourless mono-acid and dark red di-acid salts, thus:



The existence of the intermediate salts has now been established in the case of phenolsulphonphthalein, and it is also shown that other factors than the further addition of alkali which tend to increase the production of quinone-phenolate ions, such as nitration or bromination of the indicator, operate to cause intense colour changes.

For the production of phenolsulphonphthalein, "saccharin" is hydrolysed by means of dilute hydrochloric acid (400 grams; 500 c.c. conc. HCl; 6-7 litres of water), and the ammonium hydrogen *o*-sulphobenzoic acid is allowed to crystallise after concentration (to 600 c.c.). The salt is finely powdered, thoroughly wetted with thionyl chloride, and heated for a few hours, when the excess of reagent is distilled off under reduced pressure and the residual cake is broken up and extracted with benzene. The pure *o*-sulphobenzoic anhydride is heated with phenol at 130-135° for six hours, when the excess of phenol is removed in steam, the residue is dissolved in alkali hydroxide, filtered, and the phenolsulphonphthalein is precipitated by an acid.

Phenolsulphonphthalein dissolves in boiling water to the extent of about 0.03 gram per 100 c.c. The solution is orange-coloured, since it contains the free quinonoid sulphonic acid. On the addition of pure sodium hydroxide solution, a purple streak appears locally, but this disappears on shaking, and is not permanent until nearly one equivalent of alkali has been added. That is, a salt of the quinonoid sulphonic acid is being formed having the same colour as the acid, and at last, when the ionisation of the sulphonic group is so depressed that phenolate ions appear, then the striking colour change takes place. The changes are represented thus:



The *mono-potassium*, *mono-silver*, and *mono-calcium* salts have been isolated; they all give orange solutions, which become purple

on the addition of alkali hydroxides. When left in an atmosphere of ammonia, phenolsulphonphthalein also forms an almost black ammonium salt, which dissolves with purple colour, and changes into a red mono-ammonium salt when left over sulphuric acid in a desiccator.

Tetrabromophenolsulphonphthalein is conveniently obtained by slowly adding bromine to a solution of the indicator in acetic acid maintained near its boiling point. The crystals are almost colourless when moistened with acetic acid, but acquire a flesh-pink colour when dried. When heated, it gives a green sublimate at 210° , becomes deeper orange in colour, and finally melts at $270-271^{\circ}$ (decomp.). The *di-ammonium* salt is stable in the neighbourhood of sulphuric acid, owing to the increased acidity of the phenol group. *Tetranitrophenolsulphonphthalein*, canary-yellow, minute flakes, decomp. above 200° , also forms a stable *di-ammonium* salt. The tetrabromo-compound dissolves in water (0.7 gram per litre), giving a dark red solution, which becomes deep blue on diluting or adding a trace of alkali, but gradually yellow on adding a strong acid. The tetranitro-compound gives purple-red solutions in water, which are not visually or spectroscopically altered by the addition of small amounts of alkali, but gradually become yellow on adding acids, the solution changing to purple once more on dilution. Owing to the presence of nitro-groups or bromine atoms in the phenolic components, the production of the coloured quinone-phenolate ions is rendered easy, and considerable concentrations of hydrogen ions must be present before their ionisation is depressed.

Phenolsulphonphthalein and its tetrabromide have been treated with diazomethane. The products, m. p. 158° and m. p.

$234-235^{\circ}$, appear to be esters of the type $\text{SO}_3\text{Me}\cdot\text{C} \begin{smallmatrix} \swarrow \text{C}_6\text{H}_4\cdot\text{O} \\ \searrow \text{C}_6\text{H}_4\cdot\text{OMe} \end{smallmatrix}$ but they are remarkably stable towards alkalis, and must be investigated more fully.

It is stated that stannic chloride is an excellent agent for the condensation of phthalic anhydride and phenols.

J. C. W.

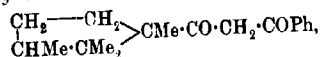
Optically Active Ketones : Ketones of 1:2:2:3-Tetramethylcyclopentane. H. RUPE and C. A. KLOPFENBURG (*Helv. Chim. Acta*, 1919, 2, 363-378).—1-Acetyl-1:2:2:3-tetramethylcyclopentane (1:2:2:3-tetramethylcyclopentyl methyl ketone).

$\text{CH}_3\text{Me} \begin{smallmatrix} \swarrow \text{CHMe}\cdot\text{CH}_3 \\ \searrow \text{CMe}_2\cdot\text{Ac}\cdot\text{CH}_3 \end{smallmatrix}$, prepared by treating the chloride of camphoric acid (1:2:2:3-tetramethylcyclopentane-1-carboxylic acid) with either zinc methyl or ethyl sodiummalonate or ethyl sodiumacetacetate, and purified by means of its semicarbazone, is a colourless, mobile oil with a persistent cedar-wood oil odour, b. p. $83-95^{\circ}/10$ mm., D_4^{20} 0.9163, $[\alpha]_D^{20} + 51.27^{\circ}$, $[\alpha]_D^{25} + 63.67^{\circ}$, $[\alpha]_D^{30}$ ($\lambda = 546.3 \mu\mu$) $+ 74.17^{\circ}$, and $[\alpha]_D^{30} + 93.32^{\circ}$; in benzene solution these rotations are respectively 43.45° , 53.89° , 62.06° , and 77.49° . The semicarbazone has m. p. 226° (decomp.) (Meerwein, this vol., 1, 162, gave m. p. 232°); the oxime, m. p. 69.5° , the *p*-nitrophenyl-

hydrazone, m. p. 134° , the benzylidene derivative, m. p. 45° , D_4^{20} 0.8896, $[\alpha]_D^{20} + 44.29^{\circ}$, $[\alpha]_D^{25} + 54.29^{\circ}$, $[\alpha]_{H_2}^{20} + 61.49^{\circ}$, $[\alpha]_D^{25} + 69.36^{\circ}$ (in benzene), and the antyldene derivative, m. p. 54° , D_4^{20} 0.8924, $[\alpha]_D^{20} + 50.65^{\circ}$, $[\alpha]_D^{25} + 63.43^{\circ}$, $[\alpha]_{H_2}^{20} + 74.07^{\circ}$, $[\alpha]_D^{25} + 90.54^{\circ}$, were prepared.

1:2:2:3-Tetramethylcyclopentyl ethyl ketone, $C_{12}H_{22}O$, prepared by the action of either zinc ethyl iodide or zinc ethyl on the acid chloride of 1:2:2:3-tetramethylcyclopentane-1-carboxylic acid, forms a colourless oil of aromatic odour, b. p. $104^{\circ}/10$ mm., D_4^{20} 0.9124, $[\alpha]_D^{20} + 50.64^{\circ}$, $[\alpha]_D^{25} + 63.15^{\circ}$, $[\alpha]_{H_2}^{20} + 73.89^{\circ}$, $[\alpha]_D^{25} + 94.08^{\circ}$. It does not condense with semicarbazide or hydroxylamine, but yields a p-nitrophenylhydrazone, m. p. 201° .

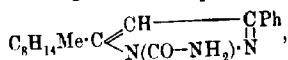
1-Benzoylacetyl-1:2:2:3-tetramethylcyclopentane,



prepared either by the condensation of ethyl 1:2:2:3-tetramethylcyclopentane-1-carboxylate with sodioacetophenone or by the action of ethyl benzoate on 1:2:2:3-tetramethylcyclopentyl methyl ketone, forms a viscous, yellow, odourless oil, b. p. $205^{\circ}/10$ mm., D_4^{20} 1.0500, $[\alpha]_D^{20} + 50.19^{\circ}$, $[\alpha]_D^{25} + 63.83^{\circ}$, $[\alpha]_{H_2}^{20} + 76.08^{\circ}$, $[\alpha]_D^{25} + 100.92^{\circ}$; in benzene, the respective rotations are 45.07° , 57.26° , 68.22° , and 90.25° . Its alcoholic solution gives an intense red coloration with ferric chloride. With phenylhydrazine it forms the diphenylated

pyrazole, $C_8H_{14}Me \cdot C \begin{array}{c} \text{CH} : \text{CPh} \\ | \\ \text{N} - \text{NPh} \end{array}$ or $C_8H_{14}Me \cdot C \begin{array}{c} \text{CH} - \text{CPh} \\ | \\ \text{NPh} \cdot \text{N} \end{array}$, which crystallises in long, white, felted needles, m. p. 142° , and becomes highly electrified when rubbed. With semicarbazide it gives the

compound, $C_8H_{14}Me \cdot C \begin{array}{c} \text{CH} : \text{CPh} \\ | \\ \text{N} - \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{array}$ or



which forms short, apparently monoclinic, white prisms.

A simple method of preparing zinc methyl in large quantities by the action of a zinc-copper couple on methyl iodide in a steel bomb is described.

T. H. P.

Relations between the Ionones and Irons. L. RUZICKA (*Helv. Chim. Acta*, 1919, 2, 352-363).—The reduction of iron by hydrogen in presence of colloidal palladium or platinum black yields tetrahydroiron, an exact chemical proof being thus furnished of the presence of two double linkings in the iron molecule. According to the formulæ for α - and β -ionones and iron, the tetrahydro-derivatives of these compounds should be identical, except as regards optical activity. The two ionones do, indeed, yield the same tetrahydro-product (compare Skita, A., 1913, i, 63), but tetrahydroiron differs from this, not only by its dextro-rotation, but by its higher density and higher boiling point. Assuming the same structural formula, such differences can depend only on *ch*

trans isomerism; the boiling-point difference, namely, $14^{\circ}/13$ mm., is higher than has been observed in any similar case, and may be conditioned by the relatively long side-chain of the molecules.

The attempts made to establish the structural relations between tetrahydroionone and tetrahydroirone have been unsuccessful. The latter does not undergo racemisation when heated at a high temperature with either hydrochloric acid or alkali. Further, oxidation of the saturated ketones by means of permanganate, as well as oxidation by means of sodium hypobromite of the sodium salts of tetrahydro-iononic and -ironic acids, do not yield the expected products, the formation of large proportions of oxalic acid in all cases indicating that the long side-chain is first oxidised away. Results previously obtained, especially the reaction by which β -ionone is formed, and which consists in the scission of a water molecule, indicate that in the ionones (and tetrahydroionone) the two side-chains, CH_3 and $\text{CH}:\text{CHAc}$, occupy *cis*-positions and in irone (and tetrahydroirone) *trans*-positions at the asymmetric carbon atom.

When irone is reduced in presence of colloidal palladium by means of a limited proportion of hydrogen, only tetrahydro- and not dihydro-irone is formed, and it is uncertain if Skita (*loc. cit.*) obtained dihydroionones in this way, no crystalline derivatives being described by him.

Tetrahydroirone, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2-\text{CMe}_2 \\ \text{CH}_2-\text{CHMe} \end{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COMe}$, forms a colourless oil of characteristic cedar-wood odour, b. p. $143-145^{\circ}/15$ mm., and in carbon disulphide solution decolorises bromine with evolution of hydrogen bromide. The *semicarbazone*, $\text{C}_{14}\text{H}_{27}\text{ON}_3$, forms crystals, m. p. $202-203^{\circ}$, and gives the ketone again when boiled with potassium hydrogen sulphate solution.

Tetrahydroionol, b. p. $142-143^{\circ}/17$ mm., D^{15}_D 0.9144 (Skita, A., 1916, i, 16, gave b. p. $142-143^{\circ}/20$ mm., D^{20}_D 0.9126), may be obtained by reducing the ionones by means of hydrogen in ethereal solution containing platinum black, whereas in presence of colloidal palladium the reduction proceeds only as far as tetrahydroionone.

Reduction of α -ionone in 50% aqueous-alcoholic solution by means of hydrogen in presence of Kelber's nickel catalyst (A., 1916, ii, 369) yields *dihydroionol* as an oil, b. p. $135-140^{\circ}$, so that in this case the reduction of the carbonyl group precedes that of one of the double linkings, probably that in the ring; this appears to be the first instance of such a reaction (compare Rupe, Werder, and Takagi, this vol., i, 27). Dihydroionol does not form a *semicarbazone*, and on oxidation is converted into *dihydroionone*, $\text{C}_{13}\text{H}_{22}\text{O}$, which is a mobile liquid, b. p. $130-132^{\circ}/14$ mm., and yields the *semicarbazide*, $\text{C}_{14}\text{H}_{25}\text{ON}_3$, m. p. $166-168^{\circ}$.

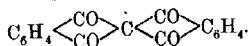
Tetrahydroironic acid, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2-\text{CMe}_2 \\ \text{CH}_2-\text{CHMe} \end{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, has b. p. $185-190^{\circ}/15$ mm., m. p. (crude) about 80° , and *tetrahydroiononic acid*, of the same structural formula, is a viscous oil, b. p. $173-178^{\circ}/12$ mm.

T. H. P.

Diketohydrindene. III. ANANDA KISORE DAS and BROJENDRA NATH GHOSH (*J. Amer. Chem. Soc.*, 1919, **41**, 1221—1225. Compare T., 1915, **107**, 1442; 1916, **109**, 175).—When diketohydrindene is condensed with certain acid anhydrides in the presence of concentrated sulphuric acid, complex, sparingly soluble compounds are formed, which may also be prepared by condensing the anhydrides with anhydrobisdiketohydrindene (Wislicenus and Kötze, A., 1889, 1067), this being, therefore, the primary product in the first reaction. Thus, phthalic anhydride gives the compound, $C_{25}H_{12}O_8$, which crystallises from nitrobenzene in lustrous flakes, m. p. 320° ; benzoic anhydride yields the compound, $C_{25}H_{12}O_8$, golden-yellow needles, m. p. above 320° ; and succinic anhydride forms the compound, $C_{21}H_{10}O_8 \cdot H_2O$, which sublimes without melting at above 316° . The compounds dissolve in hot aniline without forming anilides.

The condensation of diketohydrindene with phthalic anhydride in the presence of acetic anhydride has been described by Marches (A., 1907, i, 941), who obtained a compound, $C_{26}H_{12}O_8$. This is similar to the above compound, $C_{25}H_{12}O_8$, in outward appearance and m. p., but it differs in that it dissolves freely in sodium hydroxide and is changed on boiling with aniline into a black, crystalline substance, $(C_8H_6O)_x$, m. p. 110° .

The experiment with phthalic anhydride was undertaken in the hope of obtaining a compound of the formula



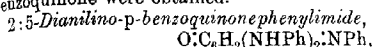
To this end, ethyl phthalate was made to react with diketohydrindene in the presence of sodium ethoxide, but the product was, Schwerin's 2-benzoyl-1:3-diketohydrindene (A., 1894, i, 19; mixed with a little anhydrobisdiketohydrindene. J. C. W.

Indophenols and Indamines. II. GUSTAV HELLER (*Annalen*, 1919, **418**, 259—274. Compare A., 1912, i, 916).—It has long been known that indophenols are decomposed by hot dilute mineral acids in the sense of the equation $O:C_6H_4:N \cdot C_6H_4 \cdot OH + H_2O = O:C_6H_4:O + NH_2 \cdot C_6H_4 \cdot OH$. A further change occurs, however, when contact with the mineral acid is maintained for many hours, $2O:C_6H_4:O + 2NH_2 \cdot C_6H_4 \cdot OH = C_6H_4(OH)_2 + O:C_6H_4(NH \cdot C_6H_4 \cdot OH)_2$.

so that the final main products are quinol and dianilinoquinones. The complex substance obtained by the action of hydrochloric acid on the simplest indophenol (*loc. cit.*) is now shown to be 2:5-di-*p*-hydroxyanilino-*p*-benzoquinone by its formation from *p*-benzoquinone and *p*-aminophenol in aqueous-alcoholic solution. In a similar manner, toluquinone yields di-*p*-hydroxyanilino-*p*-toluquinone, brown needles, which do not melt below 290° , and *p*-benzoquinone and *as*-dimethyl-*p*-phenylenediamine yield 2:5-di-*p*-dimethylaminoanilino-*p*-benzoquinone. The last compound is not obtained in the decomposition of phenol-blue by hydrochloric acid, because the

dimethylamino-group is replaced by hydroxyl and 2:5-di-*p*-hydroxylanilino-*p*-benzoquinone is formed.

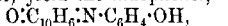
The course of the decomposition of indophenols described above was first elucidated by an investigation of the action of hydrochloric acid (*N*/5) on Bandrowski's base, *p*-benzoquinone-*p*-tolylimide, $\text{O}:\text{C}_6\text{H}_4:\text{N}:\text{C}_6\text{H}_4$, whereby quinol and 2:5-di-*p*-toluidino-*p*-benzoquinone were obtained.



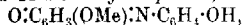
m. p. 202—203°, and 2:5-dianilino-*p*-benzoquinone-*p*-tolylimide, reddish-brown leaflets, m. p. 214°, are obtained by treating *p*-benzoquinonephenylimide and *p*-benzoquinone-*p*-tolylimide respectively with an alcoholic solution of aniline containing a little acetic acid.

After contact with dilute sulphuric acid for three days, Bind-schedler's green yields, amongst other products of the decomposition, tetramethylbenzidine, produced probably by the oxidising action of *p*-benzoquinone on dimethylaniline formed in the reaction.

By oxidation with an alkaline solution of sodium hypochlorite at -10° to -15°, α -naphthol and *p*-aminophenol (but not phenol and 4-amino- α -naphthol) yield the *indophenol*,



crystalline powder, which forms two isomeric *monoanilino*-derivatives, $\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$, m. p. 256° and 181° respectively; guaiacol and *p*-aminophenol yield 11-methoxyindophenol,

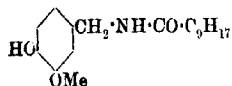


m. p. 181—182° (decomp.) (9:12-dianilino-derivative, m. p. 208—209°), and *m*-chlorophenol and *p*-aminophenol yield 1-chloroindophenol, m. p. 156° (sodium derivative, $\text{C}_{12}\text{H}_7\text{O}_2\text{NClNa}$, needles); the dianilino-derivative, $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_2\text{Cl}$, bronze-green needles, m. p. 211—212°, of the last compound is oxidised in alcoholic solution at 60° to the *dianil*, red prisms, m. p. 212—213°, by chromic and acetic acids.

4-Anilino-4'-hydroxydiphenylamine, $\text{NHPh}:\text{C}_6\text{H}_4:\text{NH}:\text{C}_6\text{H}_4:\text{OH}$, very scales, m. p. 145°, is obtained by heating a mixture of aminodiphenylamine, quinol, and zinc chloride at 180°; a portion of the product can be purified by crystallisation, but the main portion, apparently in consequence of oxidation, must be reduced in alcoholic solution by zinc dust and glacial acetic acid before it is recrystallised. By treating its solution in boiling benzene with mercuric oxide, the substance is oxidised to 3-anilinoindophenol, $\text{CC}_6\text{H}_4:\text{N}:\text{C}_6\text{H}_4:\text{NHPh}$, bluish-violet crystals containing 1 mol. HCl , m. p. 158°. C. S.

The Constitution of Capsaicin, the Pungent Principle of Capsicum. E. K. NELSON (*J. Amer. Chem. Soc.*, 1919, 41, 115—1121).—The amount of capsaicin in cayenne pepper varies considerably, a very good sample yielding, when treated according to Micko's method (*A.*, 1899, i, 716; see also Nelson, *A.*, 1911, ii, 551), about 60 grams of the pure substance per 50 kilos.

The compound is now shown to be a condensation product of vanillylamine and a decenoic acid (annexed formula).



Capsaicin crystallises from a mixture of light petroleum and ether (9:1) in monoclinic plates (α , 1'520; β , 1'540; γ , 1'580), m. p. 65°. Its methyl ether forms bundles of minute needles (α , 1'55; β , 1'58; γ , 1'60), m. p. 77—78°, and is only slightly pungent. On oxidation with alkaline permanganate, this ether yields veratric acid, and when hydrolysed by means of methyl-alcoholic hydrochloric acid, it gives 3:4-dimethoxybenzylamine hydrochloride, which crystallises in monoclinic rods or narrow plates (α , 1'505; β , 1'670; γ , 1'700) (compare Juliusberg, A., 1907, i, 219). Capsaicin itself yields 4-hydroxy-3-methoxybenzylamine hydrochloride (see below) when hydrolysed in the same way, but hydrolysis with 25% sodium hydroxide at 180° enables the acid fragment to be isolated in excellent yield. The alkaline liquid is saturated with carbon dioxide, extracted with ether to remove the decomposition products of the amine residue, the aqueous portion is then evaporated to dryness, the organic salt is separated by means of boiling alcohol, and finally decomposed by dilute sulphuric acid. The acid appears to be a new decenoic acid, $\text{C}_{10}\text{H}_{18}\text{O}_2$. It has m. p. -5°, b. p. 258—261°/atm. (corr.), forms a dibromide, m. p. 57—59°, and an amide, pearly leaflets, m. p. 96—97° (corr.), which differs from the amides of two decenoic acids described by Wallach, and the saturated *decoic acid* obtained by Paal's method has b. p. 260°, m. p. 24—25°, and immediately causes the liquefaction of decoic acid from coconut oil (compare Lapworth and Royle, T., 1919, 115, 1109).

The base, *vanillylamine* (4-hydroxy-3-methoxybenzylamine), was prepared for comparison by the reduction of vanillin oxime. It is very unstable, crystallises from water in slender needles, m. p. 131—133° (after drying at 110°), and yields a *hydrochloride*, colourless rods (α , 1'510; β , 1'705; γ , 1'735). J. C. W.

Solubility of Carbon Dioxide in Solutions of Chlorophyll.

ROBERT KREMANN and NORBERT SCHNIDERSCHITSCH (*Monatsh.*, 1916, 37, 659—679).—With the object of ascertaining whether chlorophyll and carbon dioxide form an additive compound in the assimilation of the latter by the leaves of trees, the authors have determined the solubility of carbon dioxide in 95% alcoholic solutions of chlorophyll both in the absence and the presence of light. The experiments were carried out both by the static method and the dynamic method. In the latter method, the amount of carbon dioxide dissolved was estimated by determinations of the electrical conductivity of the solutions. A similar series of experiments was also carried out with 95% alcohol which contained no chlorophyll. The experiments show that the solubility of carbon dioxide in alcohol and in alcoholic solutions of chlorophyll is practically the same. It must therefore be concluded that neither in the dark nor in daylight is there a measurable formation of an additive compound

between carbon dioxide and chlorophyll. Further, no such compound could be observed in a colloidal suspension of chlorophyll in 45% alcohol through which carbon dioxide had been bubbled. Consequently, if such an additive compound takes any part in the absorption of carbon dioxide by living leaves, this compound can only be present in an almost unrecognisable quantity. J. F. S.

The Tannin of the Knopper Gall. MAXIMILIAN NIERENSTEIN *T.*, 1919, 115, 1174—1180).

5:6:7-Trihydroxyflavone: Constitution of Scutellarein. J. BARGELLINI (*Gazzetta*, 1919, 49, ii, 47—63).—The fact that scutellarein alone is obtained by the action of hydriodic acid on 2:3:4:6-tetramethoxyphenyl *p*-methoxybenzoylmethyl ketone, which thus undergoes demethylation and also loses 1 mol. of water, indicates that scutellarein is either 5:7:8:4'- or 5:6:7:4'-tetrahydroxyflavone (*A.*, 1915, i, 84). The decision between these two constitutions is now made as follows. By condensation with methyl benzoate in presence of sodium, 2:3:4:6-tetramethoxyphenyl methyl ketone is converted into 2:3:4:6-tetramethoxyphenyl benzoylmethyl ketone, and hydrolysis of the latter by means of hydriodic acid, as above, yields a trihydroxyflavone, which may be either the 5:7:8- or the 5:6:7-derivative; as this compound is different from the 5:7:8-trihydroxyflavone (hydroxychrysin) described by Nierenstein (*A.*, 1912, i, 292), it must be regarded as 5:6:7-trihydroxyflavone. On the assumption that the elimination of water in the formation of scutellarein from 2:3:4:6-tetramethoxyphenyl *p*-methoxybenzoylmethyl ketone takes place similarly to the elimination of water from benzoylmethyl 2:3:4:6-tetramethoxyphenyl ketone, scutellarein must be regarded as 5:6:7:4'-tetrahydroxyflavone (annexed formula).

Melting points different from those obtained by the author have been given by Nierenstein for certain of these derivatives. Thus, for 2:3:4:6-tetramethoxyphenyl methyl ketone, the author finds m. p. 48—50°, and Nierenstein (*T.*, 1917, 111, 4) 92—93°, and, in view of the ease with which *C*-methylated derivatives are formed when phloroglucinol and its derivatives, and also 1:2:3:5-tetrahydroxybenzene and its derivatives, are methylated, it may be that Nierenstein's so-called 2:3:4:6-tetramethoxyphenyl methyl ketone, prepared by direct methylation of the corresponding tetrahydroxy-compound, is in reality a *C*-methylated derivative.

2:3:4:6:3':4'-Hexamethoxyphenyl styryl ketone (annexed formula), obtained by condensation of 2:3:4:6-tetramethoxyphenyl methyl ketone with veratraldehyde, is a pale yellow compound, m. p. 127—128°, and dissolves in concentrated sulphuric acid with an intense red coloration.

VOL. CXVI, i.

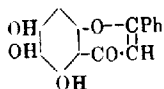
Nierenstein (*loc. cit.*) describes 2-hydroxy-3:4:6-trimethoxyphenyl methyl ketone, m. p. 125—126°, and 6-hydroxy-2:3:4-trimethoxyphenyl methyl ketone, m. p. 164—165°. The trimethylated derivative prepared by the author has m. p. 106—108°, and is probably the former of these compounds; its *acetyl* derivative, m. p. 106°, and its *benzoyl* derivative, m. p. 120—122°, have been prepared. With veratraldehyde in presence of sodium hydroxide, it yields 2-hydroxy-3:4:6:3':4'-pentamethoxyphenyl styryl ketone, m. p. 143°, as described by Nierenstein. The latter describes 2:6-dihydroxy-3:4-dimethoxyphenyl methyl ketone, m. p. 166—168°, whereas the dimethylated derivative obtained by the author has m. p. 162—163°; its *acetyl* derivative, m. p. 110—112°, has also been prepared. The tetra-, tri-, and di-methyl compounds all dissolve in concentrated sulphuric acid, giving a yellow coloration, changing to brownish-green and then to bluish-violet on heating; this colour reaction is probably common to all derivatives of 1:2:3:5-tetramethoxybenzene.

2:3:4:6-Tetramethoxyphenyl benzoylmethyl ketone,
 $C_6H(OMe)_4 \cdot CO \cdot CH_2Bz$,

forms yellow, prismatic crystals, m. p. 110—112°, and in alcoholic solution gives an intense red coloration with ferric chloride; a crystal of the compound is coloured red by concentrated sulphuric acid, the latter becoming yellow.

5:6:7-Trihydroxyflavone (annexed formula) forms a brownish-

yellow powder, m. p. about 260° (decomp.), or, when prepared from the di- or tri-acetyl derivative, shining, yellow crystals, turning brown locally at 240—250°, m. p. 262—266°. It dissolves in aqueous borax to an intense yellow solution, in concentrated sulphuric acid to a yellow solution, in sodium hydroxide solution, giving a reddish-brown solution, and in sodium carbonate solution, giving a green solution turning brownish-red. Addition of a few drops of concentrated sulphuric acid to a hot solution of the compound in glacial acetic acid yields a red, crystalline compound similar to that given under these conditions by scutellarein. Addition of a little sodium amalgam to the alcoholic solution of the trihydroxyflavone results in the deposition of green flocks; scutellarein behaves similarly, whereas 5:7:4'-trihydroxyflavone (apigenin) and 6:7-dihydroxyflavone give red colorations, and 5:7:3':4':5'-pentahydroxyflavone reddish-brown flocks. Thus, the formation of green flocks with sodium amalgam is probably a reaction characteristic of flavones containing three vicinal hydroxyl groups in the benzopyrone nucleus, and may be of service as an indication of the constitution of other natural flavones or flavonols. The *diacetyl* derivative of 5:6:7-trihydroxyflavone, $C_{18}H_{14}O_7$, forms yellow needles, m. p. 198—200°, and gives a red coloration with ferric chloride in alcoholic solution. The *triacetyl* derivative, $C_{21}H_{16}O_8$, forms white needles, m. p. 190—192°, and dissolves in concentrated sulphuric acid to a yellow solution, but gives no coloration with ferric chloride in alcoholic solution. The (6:7-?) *dimethyl ether*,



$C_{17}H_{14}O_5$, forms yellow needles, m. p. 155—156°, and with ferric chloride in alcoholic solution gives a red coloration changing to green with excess of the reagent. The trimethyl ether, $C_{18}H_{16}O_5$, forms light, wool-like needles, m. p. 165—166°, and dissolves to a yellow solution in concentrated sulphuric acid, but gives no coloration with ferric chloride in alcoholic solution.

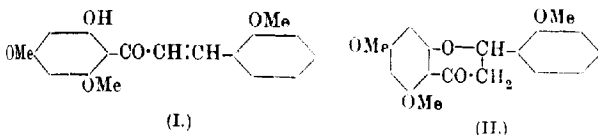
T. H. P.

5:7:2'-Trihydroxyflavanol: Synthesis of Datisctetin.

G. BARGELLINI and E. PERATONER (*Gazzetta*, 1919, **49**, ii, 64—69).

5:7:2'-Trihydroxyflavanol has been prepared as follows. Condensation of 2-hydroxy-4:6-dimethoxyphenyl methyl ketone with the methyl ether of salicylaldehyde in presence of sodium hydroxide yields 2-hydroxy-4:6:2'-trimethoxyphenyl styryl ketone, which, when boiled with dilute hydrochloric acid in alcoholic solution, is converted partly into 5:7:2'-trimethoxyflavanone. Treatment with amyl nitrite transforms the latter into its isonitroso-derivative, and this, when heated with dilute sulphuric acid in acetic acid solution, gives 5:7:2'-trimethoxyflavanol. The latter should be identical with the trimethyl ether of the datiscetin of Marchlewski and Korczyński (*A.*, 1907, i, 435), and should yield datiscetin (5:7:2'-trihydroxyflavanol) when treated with hydriodic acid, but lack of material has prevented the completion of the work.

2-Hydroxy-4:6:2'-trimethoxyphenyl styryl ketone (I) forms

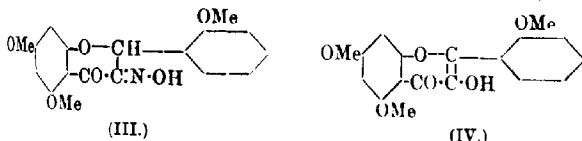


canary-yellow crystals, m. p. 106—108°, and dissolves in concentrated sulphuric acid with an orange-red coloration.

5:7:2'-Trimethoxyflavanone (II) crystallises in white needles, m. p. 124—125°, and dissolves in concentrated sulphuric acid to a brownish-yellow solution.

2-Oximino-5:7:2'-trimethoxyflavanone (III) forms pale yellow crystals, m. p. 189—190° (decomp.).

5:7:2'-Trimethoxyflavanol (IV) crystallises in pale yellow

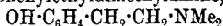


needles, m. p. 158—160°, and dissolves in concentrated sulphuric acid, giving a yellow solution which exhibits intense green fluorescence. Datisctetin also gives a fluorescent solution in sulphuric acid.

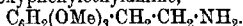
T. H. P.

The Anhalonium [Cactus] Alkaloids. I. Anhaline and Mezcaline. ERNST SPÄTH (*Monatsh.*, 1919, 40, 129—154).—

The cactus alkaloids have been investigated most completely so far by Heffter (A., 1895, i, 120; 1896, i, 267; 1898, i, 499; 1901, i, 736; 1905, i, 877), and seven bases are described in the literature, namely, anhaline, mezcaline, peliotine, anhalonidine, anhalonine, anhalamine, and lophophorine. These have about the same physiological properties (Mogilewa, *Arch. expt. Path. Pharmac.*, 1903, 49, 137) and are closely related chemically. It is now shown that anhaline is identical with the hordenine of barley germs, that is, it is β -*p*-hydroxyphenylethyldimethylamine,

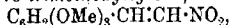


(Léger, A., 1906, i, 204, 761; Rosenmund, A., 1910, i, 241), and mezcaline has been synthesised by a method which shows that it is β -3:4:5-trimethoxyphenylethylamine,



Anhalonine and lophophorine each contain a methoxy-group and two non-hydroxylic oxygen atoms, but the other bases are simply methylated members of the 3:4:5-trihydroxyphenylethylamine series.

Synthesis of Mezcaline.—Gallic acid is methylated by means of methyl sulphate, and then converted into 3:4:5-trimethoxybenzoyl chloride by the action of phosphorus pentachloride. This is reduced in boiling toluene by hydrogen in the presence of palladised barium sulphate, the yield of 3:4:5-trimethoxybenzaldehyde being good, although some by-products are formed (Rosenmund, A., 1918, i, 300). The aldehyde is condensed with nitromethane to form ω -nitro-3:4:5-trimethoxystyrene,



long, yellow needles, m. p. 120—121°, and this is reduced by means of zinc dust and acetic acid to an oxime, and then by sodium amalgam to β -3:4:5-trimethoxyphenylethylamine, which is a colourless, highly refractive, viscous oil having b. p. 180—180.5°/12 mm. and a faint, basic odour. The procedure at all these stages is that devised by Rosenmund (A., 1910, i, 110). The base gives the following derivatives, which are identical with those obtained from a specimen of Merck's mezcaline, and already described in part by Heffter; *sulphate*, $\text{B}_3\text{H}_5\text{SO}_4 \cdot 2\text{H}_2\text{O}$, long, glistening prisms, m. p. 183—186°; *picrate*, yellow crystals, m. p. 216—218°; *platinichloride*, rosettes of straw-yellow needles, m. p. 187—188°; *aurichloride*, $\text{B}_3\text{HAuCl}_4 \cdot \text{H}_2\text{O}$, orange needles, decomp. 140—141°; *benzoyl derivative*, m. p. 120—121°; *m-nitrobenzoyl derivative*, m. p. 161—162°; *quaternary methiodide*,



m. p. 224—225°.

Heffter found on analysis that mezcaline behaves as though it contains a methylamino-group, $-\text{NHMe}$, and this is confirmed. The explanation seems to be that some rearrangement in the molecule proceeds during the analysis, for Heffter himself disposed of the alternative formula, $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CH}_2 \cdot \text{NHMe}$. Still another alternative, $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CHMe} \cdot \text{NH}_2$, is now negated by the

synthesis of the base with this formula. 3:4:5-Trimethoxyphenyl methyl ketone (Mauthner, A., 1910, i, 680) is converted into the oxime, needles, m. p. 102—103°, and this is reduced by means of sodium amalgam. α -3:4:5-Trimethoxyphenylethylamine is a strong base which forms a solid carbonate on exposure to the air. Its benzoyl derivative has m. p. 150—151°, and the quaternary methiodide, $C_6H_2(OMe)_3 \cdot CHMe \cdot NMe_3I$, melts at 180—182°, then resolidifies, melts again at 235—237°, and decomposes at 250—255°.

J. C. W.

Some Cases of Solubility Influence. II. Compounds of Caffeine existing in Aqueous Solution. G. BARGELLINI (*Gazzetta*, 1919, 49, i, 191—200).—Cryoscopic investigation of solutions containing caffeine, together with either antipyrine, sodium benzoate, resorcinol, quinol, or catechol gives results indicating the formation of compounds between the solutes, the solubility of the caffeine being apparently increased. With phloroglucinol or pyrogallol, however, caffeine appears to form compounds exhibiting but slight solubilities in water (compare Ultée, A., 1910, i, 132). The solubility of caffeine in water is about 1%, in 10% resorcinol solution about 3%, and in more concentrated resorcinol solutions still more.

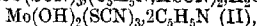
T. H. P.

Compound of Yohimbine containing Arsenic. W. GRÜTTFELN (U.S. Pat. 1305462).—Arsenic acid (150.7 parts) and yohimbine (368 parts) are dissolved in water (1000 parts). The solution is filtered and evaporated, the residue is mixed with acetone, and the salt thus obtained is filtered and dried at 100°. Yohimbine arsenate thus produced forms an almost colourless powder, m. p. 243°. Yohimbine methylarsinate, m. p. 203°, is obtained from methylarsinic acid (130 parts) and yohimbine (368 parts). Yohimbine phenylarsinate, m. p. about 140°, is produced by the interaction of phenylarsinic acid (202 parts) and yohimbine (368 parts) dissolved in alcohol (1000 parts). Yohimbine chloroarsobenzoate is a faintly coloured powder, m. p. about 90°, soluble in water, alcohol, and acetone. It is produced from chloroarsobenzoic acid (462.5 parts) and yohimbine (368 parts) dissolved in acetone (10,000—15,000 parts). If necessary, the solution is filtered and the filtrate carefully evaporated. The viscous paste which is at first obtained becomes solid after keeping for a short time in a desiccator, and can then be easily pulverised. These compounds are stated to be especially suitable as therapeutic agents because they do not possess the pronounced irritating effect on the intestine which is common both to arsenic compounds generally and to yohimbine.

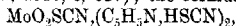
CHEMICAL ABSTRACTS.

Colour Reactions of Molybdenum and Tungsten. I. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 351—355).—According to Sand and Burger (A., 1905, i, 923; 1906, i, 487), and Rosenheim and Koss (A., 1906, i, 603), the action of pyridine on the red and violet liquids obtained from an acidified solution

containing a molybdate and a thiocyanate, either by boiling or by treating in the cold with zinc, tin, or other reducing agent, yields the compounds $\text{MoO}(\text{SCN})_3(\text{C}_5\text{H}_5\text{N}, \text{HSCN})_2, \text{H}_2\text{O}$ (I) and

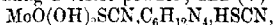


the molybdenum being quinquevalent. Since compound II is formed in acid solution, it is more probable that the pyridine unites with the thiocyanic acid, and that the molybdenum exists as molybdiyl, MoO_2 (A., 1916, i, 627); the formula,



for this compound would explain also its conversion into compound I by treatment with thiocyanic acid.

When molybdic acid is reduced in presence of thiocyanic acid (Braun's reaction, *Zeitsch. anal. Chem.*, 1863, 2, 36), the colorations produced may be due partly to sexa- and partly to quinquevalent molybdenum. The latter alone is present in molybdenyl ammonium chloride, $\text{MoOCl}_3, 2\text{NH}_4\text{Cl}$, which gives an orange-red coloration when treated, in a solution acidified with hydrochloric acid, with excess of ammonium thiocyanate; the colour changes to blood-red and then to violet on dilution or heating, further addition of water producing in succession orange-yellow and yellow colorations, and finally decolorisation. The different colours are hence the result of hydrolysis. The orange-yellow liquid gives with pyridine thiocyanate the compound I (above), whilst treatment of the coloured solutions with a hexamethylenetetramine salt under definite experimental conditions gives the compounds: (III) $\text{Mo}(\text{OH})_2(\text{SCN})_3, \text{C}_6\text{H}_{12}\text{N}_4, \text{HSCN}, 2\text{H}_2\text{O}$, black, prismatic crystals; (IV) $\text{Mo}(\text{OH})_2(\text{SCN})_3, \text{C}_6\text{H}_{12}\text{N}_4, \text{HSCN}, 2\text{H}_2\text{O}$, blackish-green crystals forming a violet powder; and (V)



orange-yellow prisms. Compounds III and IV give violet alcoholic solutions which become orange-yellow when diluted with water and heated, and, on cooling, then deposit compound V; treatment of the latter with thiocyanic acid yields a violet solution.

T. H. P.

Synthetic Investigations in the Quinine Series. I. Synthesis of β -Collidine [4-Methyl-3-ethylpyridine]. L.

RUTZICKA and V. FORNASIR (*Helv. Chim. Acta*, 1919, 2, 338—348).

—The authors have succeeded in synthesising β -collidine [4-methyl-3-ethylpyridine], the various steps in the process being as follows:

(1) Preparation of 2:6-dihydroxy- β -collidine, either by heating γ -cyano- β -methyl- α -ethylglutaconimide (5-cyano-2:6-dihydroxy-4-methyl-3-ethylpyridine) (compare Guareschi, A., 1897, i, 168) with hydrobromic acid, or by condensing ethyl ethylacetoacetate with ethyl cyanoacetate in presence of sodium and treating the cyano-glutaconic ester thus obtained with sodium hydroxide (compare Rogerson and Thorpe, T., 1905, 87, 1685); (2) conversion of the 2:6-dihydroxy- β -collidine into 2:6-dichloro- β -collidine by means of phosphoryl chloride; and (3) removal of the chlorine atoms by treatment with hydriodic acid, monochloro- β -collidine, and then β -collidine, being formed.

γ -Cyano- β -methyl- α -ethylglutaconimide has m. p. about 220° (crude) (Guareschi, *loc. cit.*, gave 234°), and its ammonium derivative, m. p. about 315° (Guareschi gave m. p. about 300°).

2:6-Dichloro-4-methyl-3-ethylpyridine, $N \begin{smallmatrix} \diagup CCl \cdot CEt \\ \diagdown CCl \cdot CH \end{smallmatrix} CMe$, is a colourless, mobile oil, b. p. 140°/12 mm., having a piercing odour and an inflammatory action on the skin.

2-Chloro-4-methyl-3-ethylpyridine, $N \begin{smallmatrix} \diagup CCl \cdot CEt \\ \diagdown CH=CH \end{smallmatrix} CMe$, forms a colourless, mobile oil with the odour of pyridine, b. p. 110°/12 mm. Its *picrate* has m. p. about 110°. T. H. P.

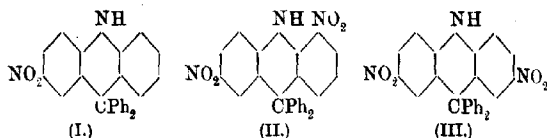
Compounds of 2-Phenylquinoline-4-carboxylic Acid with Halogen Acids. H. W. RHODEHAMEL (U.S. Pat. 1306439).—Compounds of 2-phenylquinoline-4-carboxylic acid with halogen acids are prepared by mixing the parent materials, using an excess of halogen acid, and then removing the excess of the latter by drying. The *hydriodide* forms orange-yellow crystals, m. p. 243°. It is useful as a therapeutic agent for rheumatism and gout. The *hydrobromide* forms brownish-yellow crystals, m. p. 255°. The *hydrochloride*, m. p. 223°, and *hydrofluoride* form lemon-yellow crystals. CHEMICAL ABSTRACTS.

Nitro-derivatives of 5-Diphenyldihydroacridine. F. KERHMANN, HENRI GOLDSTEIN, and PETER TSCHUDI (*Helv. Chim. Acta*, 1919, 2, 315—323. Compare A., 1918, i, 311; ii, 344).—In presence of acids, 5-diphenyldihydroacridine (compare Baeyer and Villiger, A., 1904, i, 898) is readily oxidised at the ordinary temperature by various oxidising agents, yielding coloured products with the characters of salts; the study of these products is attended with considerable difficulty. By nitric acid diluted largely with glacial acetic acid, 5-diphenyldihydroacridine is energetically attacked, with formation of crystalline nitro-derivatives, of which six have been isolated pure (see below). The corresponding amino-derivatives behave towards oxidising agents like the leuco-compounds of colouring matters, showing the characteristic properties of quinoneimide dyes and resembling particularly many azoxine dyes. The behaviour of the nitro-derivatives towards alcoholic alkali hydroxide accords with the assumption that at least one nitro-group occupies the para-position with respect to the trivalent ring nitrogen atom; they dissolve in the alkali, yielding pronounced green, red, and blue colorations, thus resembling closely the analogous nitro-derivatives of phenazoxine and thiodiphenylamine.

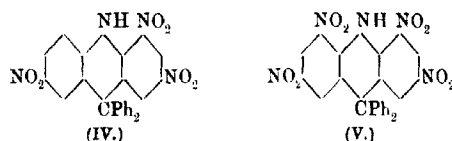
The *mononitro*-derivative of 5-diphenyldihydroacridine (I) forms compact, many-faced crystals with the colour of crystalline potassium dichromate, or, when ground, a pale orange powder, m. p. 300—301°; concentrated sulphuric acid dissolves and decomposes it, with formation of a deep blue coloration. Its *acetyl* derivative forms large, four-sided plates, m. p. 215°, yielding an

almost white powder. Addition of alkali hydroxide solution to the hot alcoholic solution yields a dichroic liquid, which is greenish-yellow in thin and purple-red in thick layers.

The *dinitro-derivative A* (formula II), forms heavy, orange-



yellow, many-faced crystals, m. p. $287-288^\circ$, giving a golden-yellow powder; its solution in alcoholic sodium hydroxide is greenish-yellow in thin and violet-brown in thick layers. The *dinitro-derivative B* (formula III) forms compact, lemon-yellow crystals with a slight blue reflex and a yellow powder with a green tinge; it begins to decompose at about 300° and has m. p. about 322.5° . Its alcoholic alkali hydroxide solution is blue in thin and deep purple in thick layers.



The *trinitro-derivative* (formula IV) forms orange-yellow leaflets containing benzene of crystallisation and a golden-yellow powder, m. p. $257-258^\circ$; its solution in alcoholic alkali hydroxide is magenta-red, and becomes reddish-violet on addition of a little water, whilst much water forms a yellow, flocculent precipitate.

The *tetranitro-derivative* (formula V) forms pale orange-yellow needles and a pale yellow powder, m. p. about 180° ; in alcoholic alkali hydroxide it gives a magenta-red solution, changing to violet on dilution.

The *hexanitro-derivative* (formula VI) forms granular, yellow crystals, m. p. $317-318^\circ$ (decomp.), and dissolves in alcoholic alkali hydroxide to a magenta-red liquid, the colour of which is unchanged by dilution.

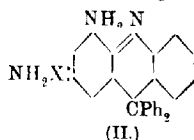
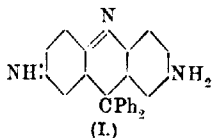
T. H. P.

Carbazine Dyes, a New Class of Quinone-imide Derivatives. F. KEHRMANN, HENRI GOLDSTEIN, and PETER TSCHUDI (*Helv. Chim. Acta*, 1919, **2**, 379-397).—The amines obtained by reduction of the nitro-derivatives prepared from 5-diphenyldi-hydroacridine (preceding abstract) behave as the leuco compound of dyes into which they are transformed by oxidation. Owing to their evident analogy to azoxine and thiazine dyes, the name

carbazine is given to these dyes. Despite their relation to acridine, carbazine dyes exhibit little similarity to the acridine dyes, the dissimilarity being sufficiently explained by the difference between the chromophores in the two cases. Like the azine, azoxine, and thiazine dyes, carbazine dyes are derivatives of quinone-di-imide, this relationship being fully borne out by their properties.

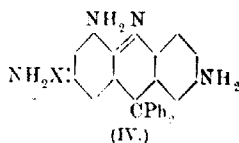
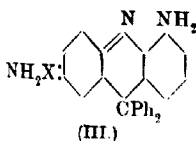
The introduction of an amino-group is accompanied by the following colour changes in the mono-acid salts: with carbazine [dihydroacridine], from yellow to bluish-green; with azoxine, from yellowish-red to bluish-violet; with thiazine, from violet-red to violet-blue, and with safranin, from violet-red to scarlet. The absolute value of the bathochromic or hypsochromic effect produced by the introduction of an amino-group into a chromogen is in general a function of the basicity of the complex it enters, the action being the more strongly bathochromic the less this basicity is developed. Thus, to explain the conversion of the bluish-green malachite-green into the bluish-violet crystal-violet by the introduction of a second *p*-dimethylamino-group, the hypothesis of colours of the second order is unnecessary. Indeed, whether the introduction of amino-groups into coloured complexes produces deepening of the colour or the reverse depends primarily on the chemical nature of the complex and secondarily on the positions assumed by the entering groups.

The quinone-imide base (formula I), corresponding with the



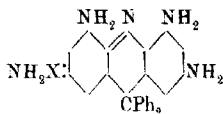
bluish-green mono-acid salts mentioned above, is yellowish-red in ethereal solution and shows a pronounced yellow fluorescence; even ammonium carbonate separates it completely from its salts. Oxidation by means of ferric chloride of the colourless leuco-diamine prepared by reduction of the yellowish-red dinitro-compound (*loc. cit.*) yields a dye (formula II or III), which, as mono-acid salt, is deep olive-green; the corresponding dark cherry-red base is even weaker than the preceding, as its salts are decomposed by sodium acetate.

Reduction of the trinitro-compound (*loc. cit.*) yields a colourless leuco-triamine, which is oxidised by ferric chloride to a colouring matter (formula IV) with an intense, pure violet mono-acid

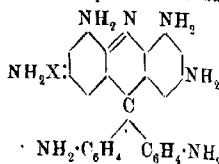


salt; the base, which is separated from its salts by ammonia, but only incompletely by ammonium carbonate, is deep orange-red, but non-fluorescent in ethereal solution. Hence the first amino-group exerts a bathochromic, but the second a hypsochromic, influence, with the limitation that the colour strength is considerably increased. Comparative dyeing tests with tannin-mordanted cotton show that the colour strength increases from the chromogen to the violet diamine, and then gradually falls until the pentamine is reached.

The leuco-tetramine gives on oxidation a pure blue mono-acid salt of the probable formula V, and the hexamine one of the probable formula VI, also blue. With both salts correspond imide bases,



(V.)



(VI.)

which are liberated from their salts only by the strongest inorganic bases, that derived from the hexamine only incompletely; boiled distilled water extracts the blue hydrates quantitatively from the violet-red ethereal solutions.

By excess of more or less concentrated acids, all the colouring matters are converted into poly-acid salts of different colour, these being mostly hydrolysed with ease by water.

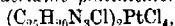
7-Amino-5-diphenylacridine salts (annexed formula) are obtained by oxidation of the leuco-compound.

7-amino-5-diphenyldihydroacridine, in acid solution by means of ferric chloride. Other solid salts are difficult to obtain, but the perchlorate, $C_{25}H_{19}N_2ClO_4$, forms a pure yellow, pulverulent, crystalline precipitate exploding when heated.

5-Diphenylacridine, $C_{25}H_{18}N_2$, forms small, pale yellow crystals decomposing without melting at 160° , and acts as a very weak base.

1(or 9):7-Diaminodiphenylacridine hydrochloride, $C_{25}H_{20}N_3Cl$, forms deep, olive-green, crystalline flocks, and the platinichloride, $(C_{25}H_{20}N_3Cl)_2PtCl_4$, small, dark green crystals. The imide base, $C_{25}H_{19}N_3$, separates, apparently as a hydrate, in deep red flocks, changing in a few minutes to fine crystals.

3:7-Diaminodiphenylacridine platinichloride,



forms metallic-green crystals, somewhat soluble in water to a greenish-blue solution. The chloride forms metallic-green crystals with the lustre of brass. The imide base, $C_{25}H_{19}N_3$, forms copper-red crystals with a golden lustre, m. p. $240-250^\circ$ (decomp.).

3:7:9-Triaminodiphenylacridine chloride, $C_{25}H_{21}N_4Cl$, forms

compact crystals with a coppery lustre, and the *platinichloride*, microscopic, blackish-violet crystals insoluble in water.

1 : 3 : 7 : 9-*Tetra-aminodiphenylacridine chloride*, $C_{25}H_{20}N_6Cl$, forms needles with a coppery lustre, and the *base*, leaflets with the lustre of bronze.

Hexa-aminodiphenylacridine chloride (formula VI), $C_{25}H_{14}N_7Cl$ forms almost black prisms with a slight metallic lustre. The base exhibits highly basic characters, and was not isolated, as it is not completely liberated from its salts by alkali hydroxide, and even in ethereal solution rapidly absorbs carbon dioxide from the air.

The constitution of these colouring matters is discussed.

T. H. P.

Derivatives of 3:5-Dinitrophenoxazine. EMIL MISSLIN and ADOLF BAU (*Helv. Chim. Acta*, 1919, 2, 285-315).—The objects of this investigation were: (1) to ascertain how far substitution in *o*-aminophenol by the radicles NO_2 , Cl , and $NHAc$ may be carried without preventing the formation of phenoxazines by the action of either picryl chloride or the more readily accessible 2:4:6-trinitroanisole in presence of an alkaline medium, and (2) to determine if in all cases the formation of phenoxazine takes place by way of an intermediate diphenylamine derivative, or if in certain cases the initial formation of a diphenyl ether is to be assumed.

The results obtained show that the action either of 2:4:6-trinitroanisole or of picryl chloride on *o*-aminophenol or its nitro-, chloro-, bromo-, or acetyl-amino-substituted derivatives of the type of picramic acid leads in presence of alkali to the formation of derivatives of 3:5-dinitrophenoxazine, diphenylamine compounds being formed as intermediate products. It is highly probable, also, that other substituted *o*-aminophenols containing the groups named, with the exception of those in which the substitution occurs in the ortho-position to the amino-group, react in the same sense with 2:4:6-trinitroanisole or picryl chloride. When suspended in alcohol, 3:5-dinitrophenoxazines substituted in the 7-position by NO_2 , Cl , Br , or $NHAc$ yield Bordeaux-red or violet colorations on addition of alkali hydroxide, whilst 3:5-dinitrophenoxazines with a nitro-group in the 6-position yield a pure blue coloration under these conditions. With simultaneous substitution in the 6- and 7-positions, the coloration is determined by the more highly negative substituent, or, if the two substituents are of similar character, by that in the 6-position. The condensation product obtained in the cold from picryl chloride and the potassium derivative of *o*-acetylaminophenol yields Turpin's 3:5-dinitrophenoxazine (T., 1891, 59, 714) on treatment with alkali.

3:5-Dinitrophenoxazine, formed from 2:4:6-trinitroanisole and *o*-aminophenol in alcoholic solution in presence of potassium hydroxide, is also obtained from the *p*-toluenesulphonic ester of 2:4:6-trinitro-2'-hydroxydiphenylamine under similar conditions, and from 2:4:6-trinitro-2'-hydroxy-*N*-acetyldiphenylamine by treatment with ammonia in alcoholic solution.

8-Chloro-3:5-dinitrophenoxazine, $C_{12}H_6O_3N_2Cl$, formed either

from 2:4:6-trinitroanisole and 4-chloro-2-aminophenol or from 5'-chloro-2:4:6-trinitro-2'-hydroxydiphenylamine *p*-toluenesulphonate, crystallises in brick-red or deep brownish-red needles. In concentrated sulphuric acid it forms a Bordeaux-red solution, which precipitates it unchanged on dilution; when suspended in alcohol, it yields a pure violet coloration with alkali hydroxide.

3:5:8-Trinitrophenoxazine, $C_{12}H_6O_7N_4$, obtained from 2:4:6-nitroanisole and 4-nitro-2-aminophenol, forms deep reddish-brown needles, and gives a Bordeaux-red solution in alkaline alcohol.

3:5-Dinitro-8-acetylaminophenoxazine, $C_{14}H_{10}O_6N_4$, prepared from 4-acetylamino-2-aminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate (compare Meisenheimer, A., 1902, i, 795), forms dark brown, velvety, felted needles. Its solution in concentrated sulphuric acid is first brownish-red and then dark red, addition of water producing a brownish-yellow precipitate. Its suspension in alcohol is coloured violet by potassium hydroxide.

3:5:9-Trinitrophenoxazine, obtained from 2:4:6-trinitroanisole and 5-nitro-2-aminophenol, was prepared by Kehrmann and Saager (A., 1903, i, 279) by nitration of 3:5-dinitrophenoxazine.

8-Chloro-3:5-dinitro-10-aminophenoxazine, $C_{12}H_7O_5N_4Cl$, obtained from 4-chloro-2:6-diaminophenol and 2:4:6-trinitroanisole, forms slender, reddish-brown, shining needles, gives a yellowish-brown solution in concentrated sulphuric acid, and yields a dull violet coloration with potassium hydroxide in alcohol.

8:10-Dichloro-3:5-dinitrophenoxazine, $C_{12}H_5O_5N_4Cl_2$, prepared from 4:6-dichloro-2-aminophenol and 2:4:6-trinitroanisole, forms small, reddish-brown, shining crystals, sparingly soluble in concentrated sulphuric acid, giving a reddish-violet coloration; in alkaline alcohol it forms a violet solution with a red tinge.

8:10-Dibromo-3:5-dinitrophenoxazine, $C_{12}H_5O_5N_4Br_2$, prepared like the corresponding dichloro-compound, forms deep reddish-brown, shining needles, and dissolves slightly in concentrated sulphuric acid with a faint blue coloration; with alcoholic alkali, a violet coloration with a red tinge is formed.

8-Chloro-3:5:10-trinitrophenoxazine, $C_{12}H_5O_7N_4Cl$, obtained from 2:4:6-trinitroanisole and 4-chloro-6-nitro-2-aminophenol, crystallises in drusy masses of matt, light brown leaflets, and gives a brownish-orange solution in concentrated sulphuric acid; its suspension in alcohol gives a violet coloration with alkali hydroxide.

3:5:8-Trinitro-10-aminophenoxazine, $C_{12}H_7O_7N_5$, prepared from 4-nitro-2:6-diaminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate (compare Meisenheimer, *loc. cit.*), crystallises in shining, reddish-brown to garnet-red needles, and dissolves readily in concentrated sulphuric acid to an intense brownish-yellow solution. In alcoholic potassium hydroxide, it dissolves incompletely to a dirty, brownish-red solution. When boiled with acetic anhydride and fused sodium acetate, it is converted into 3:5:8-trinitro-10-acetylaminophenoxazine, $C_{14}H_9O_8N_5$, which may also be obtained from 4-nitro-6-acetylamino-2-aminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate (compare Meisenheimer, *loc. cit.*), and which forms brownish-yellow leaflets

with the lustre of gold. It dissolves easily in concentrated sulphuric acid to an orange-yellow solution, and partly in alcoholic alkali hydroxide with a violet coloration showing a red tinge.

10-Chloro-3:5:8-trinitrophenoxazine, $C_{12}H_5O_7N_4Cl$, prepared from 2:4:6-trinitroanisole and 6-chloro-4-nitro-2-aminophenol, forms drusy masses of small, reddish-brown, shining crystals, and readily gives an orange solution in concentrated sulphuric acid; with alcohol and potassium hydroxide, it gives a reddish-violet to Bordeaux-red solution.

3:5:10-Trinitro-8-acetylaminophenoxazine, $C_{14}H_9O_8N_5$, obtained from 4-acetyl-amino-6-nitro-2-aminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate, forms shining, flat, pale reddish-brown needles, and gives a brownish-orange solution in concentrated sulphuric acid and a violet coloration with alkali hydroxide in suspension in alcohol.

8-Chloro-3:5:9-trinitrophenoxazine, $C_{13}H_5O_7N_4Cl$, obtained either from 2:4:6-trinitroanisole and 4-chloro-5-nitro-2-aminophenol or by nitration of 8-chloro-3:5-dinitrophenoxazine, crystallises inellar aggregates of shining, garnet-red needles, and gives a dirty, bluish-red solution in concentrated sulphuric acid and a pure blue coloration with alkali hydroxide and alcohol.

3:5:7:9-Tetranitrophenoxazine, obtained by nitration of 3:5:9-trinitrophenoxazine, agrees in properties with Kehrmann and Jaeger's preparation (*loc. cit.*).

3:5:9-Trinitro-8-methylphenoxazine, $C_{13}H_8O_7N_4$, prepared from 2:4:6-trinitroanisole and 5-nitro-2-amino-*p*-cresol, forms deep reddish-brown, shining needles, and readily dissolves in concentrated sulphuric acid to a dirty, brownish-red solution; a pure blue solution is obtained in alcohol and potassium hydroxide.

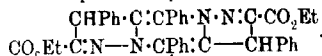
3:5:8:10-Tetranitrophenoxazine, $C_{12}H_5O_8N_5$, prepared from pyrazonic acid and either 2:4:6-trinitroanisole or picryl chloride, forms dark brown or steel-blue needles, and yields an intensely olden-yellow solution in concentrated sulphuric acid and a bluish-red solution in alcoholic alkali hydroxide.

3:5:8:9-Tetranitrophenoxazine, $C_{12}H_5O_8N_5$, prepared by nitration of 3:5:8-trinitrophenoxazine, forms long, reddish-brown leaflets with a green, metallic lustre, containing acetic acid of crystallisation, and assumes an orange-red colour when dried. It dissolves easily in concentrated sulphuric acid with an orange-red coloration, and in alcohol containing alkali hydroxide to a greenish-blue solution.

T. H. P.

Coloured Condensation Products from Ketonic Pyrazone Derivatives. E. P. KOHLER and L. L. STERLE (*J. Amer. Chem. Soc.*, 1919, **41**, 1105—1108).—The ketopyrazolines having the structure $-CO \cdot CH < NH-$ give highly fluorescent solutions in alcohol containing a trace of hydrogen chloride. Some of the products have now been isolated. They are very sparingly soluble substances of high m. p. and molecular weight, and outwardly resemble the most brilliant rhodamine dyes.

Hydrogen chloride is passed into a suspension of ethyl 5-benzoyl-4-phenylpyrazoline-3-carboxylate (this vol., i., 531) in boiling methyl alcohol, and the crimson precipitate is collected as soon as the ester has disappeared and boiled for some time with carbon disulphide. The compound, $C_{38}H_{32}O_4N_4$, is thereby changed into a mass of stout needles, m. p. 266—268°, which sublime freely at above 400° in a vacuum. It is very slightly soluble in benzene, the solution appearing a brilliant crimson-orange by reflected light and purple by transmitted light. On continuing the action of hydrogen chloride, the substance takes up water and the acid to form a yellow compound, $C_{38}H_{35}O_5N_4Cl$, plates, m. p. 258—259°, and when boiled with acetic acid for some time it combines with $2H_2O$ to give the colourless compound, $C_{38}H_{36}O_6N_4$, needles, m. p. 181°. From an approximate determination of its molecular weight, it appears that the compound may have the formula



Ethyl 5-*p*-bromobenzoyl-4-phenylpyrazoline-3-carboxylate (*ibid.*) gives a similar product, $C_{38}H_{31}O_4N_4Br$, purple-red needles, m. p. 268—270°.

Distyryl ketone reacts with ethyl diazoacetate in light petroleum at 50—70° to give ethyl 5-cinnamoyl-4-phenylpyrazoline-3-carboxylate, $\text{CHPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH} < \begin{array}{c} \text{CHPh} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{NH} - \text{N} \end{array}$, pale yellow plates,

m. p. 164.5—165°, solutions of which become blood-red with hydrogen chloride. Styryl methyl ketone yields ethyl 5-acetyl-4-phenylpyrazoline-3-carboxylate, white needles, m. p. 127°, solutions of which give an orange colour with hydrochloric acid.

Ethyl 5-acetyl-4-phenylpyrazoline-3:5-dicarboxylate, m. p. 76°, was obtained by Buchner. The present authors have obtained an isomeride with m. p. 105—106°. This gives no colour with alcoholic hydrogen chloride. J. C. W.

Asymmetric Dyes. C. W. PORTER and C. T. HIRST (*J. Amer. Chem. Soc.*, 1919, **41**, 1264—1267).—A number of dyes containing an asymmetric carbon atom have been prepared with the idea of contributing to the knowledge of vital stains, and one has been discovered on which wool acts selectively, absorbing more of the *lævo*- than the *dextro*-modification.

The parent substance is *p*-aminobenzophenone, obtained by condensing benzoyl chloride with phthalanilide in the presence of zinc chloride. This is converted into *p*-aminobenzhydrol by reduction, and into carbinols by the Grignard reaction, and these bases, containing an asymmetric carbon atom, are diazotised and coupled with (a) β -naphthol, giving dyes which are insoluble in acids, alkalis, or water, (b) dimethylaniline in the presence of about 0.1*N*-hydrochloric acid, and (c) naphtholsulphonic acids and naphthylaminesulphonic acids, to give soluble dyes.

p-Aminodiphenylmethylecarbinol, $\text{OH} \cdot \text{CMePh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, has m. p. 101°, and *p*-aminodiphenylethylecarbinol forms colourless

plates, m. p. 103°. The *dyes* mentioned in tabular form in the original are as follows: $\text{OH}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, red, m. p. 169°; $\text{OH}\cdot\text{CMePh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, red, m. p. 130°; $\text{OH}\cdot\text{CEtPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, crimson, m. p. 149°; $\text{OH}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, red, m. p. 145°; $\text{OH}\cdot\text{CMePh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, yellow, m. p. 177°; $\text{OH}\cdot\text{CEtPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, orange, m. p. 138—139°; $\text{OH}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_4(\text{SO}_3\text{H})_2\cdot\text{OH}$, red, m. p. 162°; $\text{OH}\cdot\text{CEtPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_4(\text{OH})\cdot\text{SO}_3\text{H}$, dark red, m. p. 120—122°; $\text{OH}\cdot\text{CMePh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_4(\text{OH})\cdot\text{SO}_3\text{H}$, red, m. p. 150—152°.

J. C. W.

The Constitution of Internal Diazo-oxides (Diazo-phenols).

II. GILBERT T. MORGAN and ERIC DODDRELL EVANS (T., 1919, 115, 1126—1140).

Action of Phenylhydrazine on Phthalaldehydic and Phthalonic Acids: Phenyl-hydrazo- and Azo-phthalide. PRAFULLA CHANDRA MITTER and JNANENDRA NATH SEN (T., 1919, 115, 1145—1148).

Researches on Proteins. VI. The Destructive Distillation of Fibroin. TREAT B. JOHNSON and PETER G. DASCHAVSKY (*J. Amer. Chem. Soc.*, 1919, 41, 1147—1149).—Like Pictet and Cramer (this vol., i, 227), the authors have also commenced a study of the destructive distillation of proteins, choosing in the first instance silk fibroin, because it contains no sulphur and because its chief amino-acids are well known and few in number (glycine 33%, alanine 16%, and tyrosine 10%). Distilling quantities of about 1600 grams at a time, under 25—27 mm., the authors obtain about 16% of volatile and gaseous products, soluble in sodium hydroxide or sulphuric acid, 41% of coke, and 43% of a red oil which certainly contains phenol.

J. C. W.

Application of the Kjeldahl Method to Compounds of Brucine, with Reference to the Brucine Salt of a New Nucleotide. WALTER JONES (*J. Pharm. Exp. Ther.*, 1919, 14, 489—493).—The Kjeldahl method gives exact results with salts of brucine. This fact has been applied in determining the nature of the brucine salt of a nucleotide obtained by partial oxidation of yeast-nucleic acid with potassium permanganate.

J. C. D.

Action of Enzymes on Starches of Different Origin. H. C. SHERMAN, FLORENCE WALKER, and MARY L. CALDWELL (*J. Amer. Chem. Soc.*, 1919, 41, 1123—1129).—When purified by washing with very dilute sodium hydroxide, wheat, rice, and maize starches are hydrolysable at the same rate by the same kind of amylase, and this is true for a large variety of agents, such as saliva, pancreatin, purified pancreatic amylase, malt extract, purified malt amylase, taka-diastase, or the purified amylase of *Aspergillus oryzae*. When washed with water only, potato starch

is almost pure, but the cereal starches, especially maize starch, appear to contain fatty or resinous substances which interfere with the hydrolysis, even after the starch has been dissolved in boiling water. These interfering substances are partly removed by ether, but best by dilute alkali hydroxide. Potato starch is slightly more digestible than the purified cereal starches. In one case, however, when purified potato starch was left with purified pancreatic amylase, a much lower rate of hydrolysis was observed, suggesting that some accessory substance had been removed during the purification.

The experiments on which these conclusions are based were carried out as follows. Sufficient of the starch preparations were taken to furnish 1% solutions of real, dry starch, and gelatinised by boiling with water for three minutes. The solutions were then rendered neutral to rosolic acid and made up to 100 c.c. at 40° in a thermostat. Uniform volumes of the enzyme preparations, sufficient to cause hydrolysis to proceed to about one half, were then placed with any necessary salts in several flasks and the starch solutions added. After thirty minutes at 40°, the hydrolysis was stopped by rapidly boiling the mixture, and the reducing sugar was estimated by Fehling's method. J. C. W.

The Action of Ptyalin. HUGH MCGUIGAN (*J. Biol. Chem.*, 1919, **39**, 273—284).—Chittenden and Smith (*T. Conn. Acad. Arts and Sci.*, 1885, **6**, 343) studied the action of ptyalin on starch and found that a relation between the amount of sugar formed and the amount of ptyalin used existed only when the saliva was diluted 50 to 100 times. These experiments have been in the main confirmed by the author, who has also found that the balance point shifts with the volume of saliva used, and that it may go as high as 75% of the substrate—calculated as dextrose. The products of digestion which interfere with the reaction are not dextrose or maltose. There is evidence that ptyalin combines with starch during digestion, and exerts a force which causes hydrolysis. J. C. D.

Arsenical Medical Product and Process of Producing Same. J. M. WHITE (U.S. Pat. 1297952).—A product believed to be sodium dimethylphenyl hydrogen arsenide, $C_6H_5Me_2AsHNa$, m. p. about 121°, readily soluble in water, is obtained by the interaction of sodium benzoate and sodium cacodylate in aqueous solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 847A.]

Physiological Chemistry.

Concentration of Ammonia in Blood. Comparison with Concentration of Ammonia in Different Secretions and Tissues, especially Muscle Tissue. K. L. GAD-ANDERSEN (*J. Biol. Chem.*, 1919, **39**, 267—271).—A method for the estimation of ammonia in the tissues is described. The author records that he found the concentrations of ammonia in muscle and in blood of the same order. The concentration of ammonia in the heart muscle, liver, fatty tissue, bile, cerebro-spinal fluid, and aqueous humour is the same as in blood. J. C. D.

Some Data concerning the Alleged Relation of Catalase to Animal Oxidations. RAYMOND L. STERLE (*J. Biol. Chem.*, 1919, **39**, 403—420).—The feeding of meat and the administration of "saccharin," β -hydroxybutyric acid, alanine, and glycine are not accompanied by an increase in the catalase content of the blood to the extent reported by Burge (*Amer. J. Physiol.*, 1918, **46**, 117; 1918—1919, **47**, 13). It is suggested that fluctuations in catalase content are due to fluctuations in the red cell count of the blood, and that catalase content is a function of the number of red cells. J. C. D.

Importance of Accurate and Quantitative Measurements in Experimental Work on Nutrition and Accessory Food Factors. HARRIETTE CHICK and E. MARGARET HUNE (*J. Biol. Chem.*, 1919, **39**, 203—207).—The authors point out that much of the experimental work recently published on the subject of the accessory food factors may be criticised on the ground that quantitative measurements have not received sufficient attention. In comparing the value of a series of foodstuffs as regards their value in content of some accessory food factors, it is obvious that the first step necessary is to determine in each case the minimum daily dose which will maintain health in the experimental animal, and to institute comparison between these amounts.

Neglect of this necessary procedure has led to many vague and erroneous results being reported. J. C. D.

Hydrogen- and Hydroxyl-ion Equilibrium in Solutions. I. W. LÖFFLER and K. SPIRO (*Helv. Chim. Acta*, 1919, **2**, 417—419).—Most of the liquids of the animal organism exhibit the same reaction approximating to neutrality, the maintenance of this reaction being of the utmost importance for many physiological processes, and alterations in it being of great influence on the course of essential vital processes. In an investigation of the extent to which the results obtained with colloidal solutions are applicable to solutions of crystalloids, the authors have attained a simple demonstration of the fact that the neutrality of crystalloid solu-

tions is regulated by physico-chemical as well as by chemical factors. In all adsorption processes, specific forces act, different substances showing considerable differences as regards adsorbability. Alteration of the reaction by shaking with animal charcoal is not shown by all solutions used as "moderators" or "buffers"; thus, no such change occurs with phosphate solutions, whereas with solutions of citrates and borates it is easily detectable, the value of p_H being increased with the former and diminished with the latter salts. The use to which animal charcoal is now put in the treatment of infective diseases may depend, not merely on its ability to absorb bacteria and toxins, but also on its action in combating the acidity of the stomach contents arising from bacterial influence.

T. H. P.

Equilibrium between Potassium, Rubidium, Cæsium, and Uranium. (Mlle.) L. KAISER (*Arch. Néerland Physiol.*, 1919, 3, 587—593).—Potassium in Ringer's solution may be replaced by rubidium or cæsium, as far as its action on the isolated frog's heart is concerned. The maximum action is given by the following concentrations, expressed as mg. per litre: potassium 92, rubidium 116, cæsium 78. It has been shown that certain elements, such as uranium, thorium, and radium, which should be capable of replacing potassium, actually exert an opposite effect. This is viewed in the light of the fact that potassium emits negative β -rays, whilst uranium emits positive α -rays. The antagonistic action of these elements on the frog's heart is considered.

J. C. D.

Composition of the Posterior and Anterior Lobes of Cattle Pituitaries. C. G. McARTHUR (*J. Amer. Chem. Soc.*, 1919, 41, 1225—1240).—See this vol., ii, 483.

The Supposed Occurrence of Methylguanidine in Meat, with Observations on the Oxidation of Creatine by Mercuric Acetate. ISIDOR GREENWALD (*J. Amer. Chem. Soc.*, 1919, 41, 1109—1115).—Most of the reports that methylguanidine occurs in meat are based on the use of either silver nitrate and barium hydroxide or mercuric chloride and sodium acetate as the precipitating agents. Ewins has already shown that the former agent is capable of oxidising creatine to methylguanidine (A., 1916, i, 528), and it is now proved that mercuric acetate is equally unsatisfactory, for not only does it fail to give complete precipitation, but it also oxidises creatine to methylguanidine and oxalic acid, and an intermediate product, methylguanidoglyoxylic acid, $\text{NHMe}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$. These results have recently been confirmed by Baumann and Ingvaldsen (A., 1918, i, 423).

Using a modification of the process by which Brieger isolated methylguanidine from very putrid meat in connexion with his work on ptomaines, the author has failed to find any of the base in fairly fresh meat.

J. C. W.

Metabolism of Dextrose in Surviving Organs. VII. Action of Muscular Tissue of the Dog (during Feeding and Fasting) on Dextrose Circulating in it and on the Glycogen contained in it. UGO LOMEROSO and LUDOVICO PATERNI (*Arch. farm. sper. sci. aff.*, 1919, 27, 17—32).—When placed under suitable conditions, the muscular tissue of the dog is able to consume, not merely its own glycogen, but also marked quantities of dextrose added to the liquid circulating through it, such consumption being the greater when the tissue is from a dog being fed than when it is from one kept fasting. T. H. P.

The Salicylates. XI. The Stability and Destruction of the Salicyl Group under Biological Conditions. P. J. HANZLIK and N. C. WETZEL (*J. Pharm. Exp. Ther.*, 1919, 14, 25—42).—It has been previously reported that 20 to 30% of the salicyl group remains unaccounted for after its passage through the body, and is presumably destroyed (*ibid.*, 1917, 9, 247). Solutions of sodium salicylate deteriorate when kept, particularly when they are dilute. The decomposition appears to be due to the action of living organisms, and may be inhibited by adding chloroform. Sodium salicylate solutions were found to deteriorate in the presence of yeast, but not as rapidly as when allowed to remain alone. The salicyl group appears to undergo destruction when in the presence of minced tissue. About 20% of salicylates administered to normal individuals is destroyed, whilst in the cat and dog the amount destroyed is much greater.

A general increase in metabolism, such as is encountered in febrile conditions, leads to an increased destruction of the salicyl group. J. C. D.

The Salicylates. XII. The Excretion of Salicyl after Administration of Methyl Salicylate to Animals. P. J. HANZLIK and N. C. WETZEL (*J. Pharm. Exp. Ther.*, 1919, 14, 3—46).—The excretion of salicyl by animals (dogs and cats) after the administration of methyl salicylate is approximately 25% less than after the administration of sodium salicylate. After gastric administration, the free ester was found in the urine in concentrations of 0.2 to 0.52%, and 14.4% after intramuscular injection. J. C. D.

Chemistry of Vegetable Physiology and Agriculture

Mineral Matter in Plants: The Ashes of some Roots and Tubers. LUCIEN LEROUX and DESIRÉ LEROUX (*Ann. Chim. anal.*, 919, [ii], 1, 207—209).—The following amounts of ash were found in the air-dried substances: Potato, 4.05%; common comfrey, 1.06%; dahlia, 5.10%; burdock, 12.25%; thistle, 11.45%; gentian,

3.65%; carrot, 6.25%; turnip, 7.15%; water lily, 3.65%; nettle, 7.83%; male fern, 4.83%. Analyses of the ashes are also given. The largest quantities of sulphuric acid were found in thistle ash and turnip ash (18.5% and 13.2% of SO_3 respectively); phosphoric acid was most abundant in water-lily ash (14.7% P_2O_5), and calcium in gentian ash (19.0% CaO). Gentian ash also yielded the largest quantity of iron, namely, 6.3% Fe_2O_3 . W. P. S.

Carbohydrates of Vegetables. V. Carbohydrates of Carrots. VI. Carbohydrates of Green Peas. ERNST BUSOLT (*J. Landw.*, 1916, **64**, 357—360, 361—362. Compare A., 1914, i, 792).—Carrots (6 kilos. of fresh roots) contain mannitol (23.5 grams) and dextrose (2.8 grams), whilst green peas contain mannitol, dextrose, laevulose, and glycuronic acid. T. H. P.

Secretion of Phosphates in the Stems of *Djatikapur* [*Tectona grandis*, L.]. A. WICHMANN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 968—982).—A discussion on the nature of the mineral deposits found in the stems of teak trees. From a consideration of the data the author concludes that the deposits are hydrated calcium phosphate, and that this may change into calcium magnesium phosphate. The teak tree absorbs more phosphoric acid than any other tree, and the effects of this on the nature of the soil are considered. J. F. S.

Content of Hydrastine and Berberine in *Hydrastis canadensis* Grown in Austria (at Korneuberg) and Estimation of Berberine. RICHARD WASICKY and MARIANNE JOACHIMOWITZ (*Arch. Pharm.*, 1917, **255**, 497—506).—An accurate method for estimating berberine is described, and also the results of the estimation of hydrastine and berberine in the different parts of *Hydrastis canadensis* grown in Austria. [See *J. Soc. Chem. Ind.*, 1919, 737A.] T. H. P.

The Action of some Common Soil Amendments. J. E. GREAVES and E. G. CARTER (*Soil Sci.*, 1919, **7**, 121—160).—From a review of the literature on this subject, a full bibliography of which is given, it is shown that the sulphates of magnesium, calcium, and iron, the chlorides of sodium, potassium, magnesium, and calcium, and manganese and iron salts may be especially efficient as soil stimulants. This effect is due in some cases to an increase in the available phosphate, and in others to an increase in the available nitrogen, these increases in available nitrogen and phosphorus being quite sufficient to account for the noted increase in crop yields resulting from the use of these soil amendments. In certain cases, an increase in the organic phosphorus rather than in the available phosphate or nitrogen results from their application. W. G.

General and Physical Chemistry.

Measurements in the Arc Spectrum of Iron for the Purpose of Determining Tertiary Normals. SOPHIE HOELTZENBEIN (*Zeitsch. wiss. Photochem.*, 1917, **16**, 225—251).—Making use of a concave grating, 4 metres radius and 3960 lines per centimetre, the author has re-measured the iron arc spectrum over the range $\lambda\lambda$ 5658—4859 in the third order spectrum, $\lambda\lambda$ 4315—3513 in the fourth order spectrum, and $\lambda\lambda$ 3513—2987 in the fifth order spectrum. Long tables of the wave-length and intensity of the measured lines are given, and an accuracy of about 0.001 Å. is claimed for the values of the wave-lengths. A comparison of the present results with those of Gale and Adams (*Astrophys. J.*, 1912, **35**) and St. John and Ware (*ibid.*, 1912, **36**, 14, 203) has been made, and it is shown that very many lines may be used as tertiary normals, and further, that among the lines chosen as tertiary normals very great divergencies are to be observed in the values of the different observers, and consequently more work is necessary before the tertiary normals can be finally chosen. J. F. S.

Series System in the Spectrum of Gold. W. M. HICKS (*Phil. Mag.*, 1919, [vi], **38**, 1—31).—A theoretical discussion of the series systems of the gold spectrum. It is shown that a *D* set corresponding with order $m=1$ exists, which extends far in the ultra-red, and the satellite mantissa of which conforms to the general rule of being a multiple of Δ . Gold, therefore, does not constitute an exception, as formerly appeared to be the case. It is indicated that summation lines for the *P* and *S* series exist. In general, such lines for *S* and *P* will lie far down in the ultra-violet, and this is, no doubt, one reason why they have not been previously recognised. The evidence given in the paper must be supported by further numerical coincidences obtained in other spectra before it is to be regarded as conclusive, but it is sufficient to render it extremely probable. The more accurate determination of the Δ depending on $81\delta=\Delta=113951-6p$, where 0.1p Ångström is an observational error, has been carried out. This result gives $\delta=1406.802-0.074p$. Taking the ratio of $\delta : (W/100)^2$, where *W* is the atomic weight, to be $361.75+0.05q$, the resulting value of the atomic weight of gold is $197.2024-0.0052p-0.0136q$. J. F. S.

The Constitution of the Atom and the Properties of Band Spectra. H. DENLANDRES (*Compt. rend.*, 1919, **169**, 593—599. Compare this vol., ii, 310).—A mathematical discussion in which the author shows that band spectra may be considered as formed by longitudinal and transverse vibrations, the exact part which each plays not being, as yet, fully determined. Two formulæ are deduced which account for the known facts, their

interpretation admitting of longitudinal and transverse vibrations in the atom and molecule, analogous to those in solids. W. G.

The Conditions of Excitation of Fluorescence. L. BRUNINGHAUS (*Compt. rend.*, 1919, **169**, 531—534).—The phenomena of phosphorescence and fluorescence are characterised by the fact that the maximum effect is obtained when the solution is very dilute and the exciting radiation only very feebly absorbed.

W. G.

Photochemical Change in the System $\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$, under the Influence of Light Rays of Definite Wave-length. M. LE BLANC, K. ANDRICH, and W. KANGRO (*Zeitsch. Elektrochem.*, 1919, **25**, 229—251).—A long series of experiments are described which are designed to furnish answers to the questions arising from the following case. Given an homogeneous gaseous system, $A + B \rightleftharpoons C$, which is sensitive to light and such that the absorption spectra of A , B , and C respectively do not overlap one another, and which has a zero velocity when in the dark, does the whole system become sensitive to light if it is subjected to light which is absorbed by only one constituent, and, if so, to what extent does the reaction proceed in the direction of C ? The case $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$ has been examined with the object of answering the questions. The absorption spectra of sulphur dioxide, chlorine, and sulphuryl chloride have been determined at a series of pressures, and it is shown that chlorine absorbs all light from the visible region to the middle ultra-violet, and has a maximum at $340 \mu\mu$; sulphur dioxide has an absorption maximum at $290 \mu\mu$ and a minimum at $240 \mu\mu$; sulphuryl chloride vapour absorbs light from $300 \mu\mu$ upwards. Experiments on the decomposition of sulphuryl chloride by light at a series of temperatures, the formation of gaseous sulphuryl chloride, and the formation of liquid sulphuryl chloride are described. It is shown that in the reaction $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$ the formation of secondary products does not occur to the extent of 10%. The illumination of sulphuryl chloride by light, which is practically only absorbed by this substance, brings about quantitative decomposition at both 55° and 100° . The concentration has apparently no influence on the course of the reaction. When the system $\text{SO}_2 + \text{Cl}_2$ is illuminated with light which is absorbed by sulphur dioxide, only a slight reduction of pressure takes place; this is not due to the formation of sulphuryl chloride, but to a side reaction. When the same system is illuminated by light which is only absorbed by chlorine, the formation of sulphuryl chloride takes place until, after a time, a stationary condition is set up. The velocity and also the position of the stationary condition depend, at constant temperature, on the presence of a small quantity of water, and the higher the temperature the earlier the stationary condition is reached. In a number of cases a reversal is noted, so that the stationary condition does not come at the end of diminution of pressure, but of an increase in pressure. At the temperatures 105° and 125° , at which the equili-

brium in the dark is known, the stationary condition lies more to the side of sulphuryl chloride than in the non-illuminated reaction. Under none of the experimental conditions do the two points coincide. The lower the temperature the further apart are the end-points of the illuminated and the non-illuminated reactions. The temperature-coefficient of the formation of sulphuryl chloride from chlorine and sulphur dioxide by light which is only absorbed by chlorine is small, and has little influence on the course of the reaction.

J. F. S.

Photochemical Reactions of Compounds of Less Common Elements. II.

ALFRED BENRATH (*Zeitsch. wiss. Photochem.*, 1917, 16, 253—261. Compare A., 1915, ii, 504).—An aqueous solution of ammonium molybdate when diluted with an equal volume of either ethyl alcohol or methyl alcohol and exposed to sunlight changes to blue after a short exposure and a reddish-brown substance is deposited on the side of the flask on which the light falls. This compound has the formula $(\text{NH}_4)_2\text{MoO}_4 \cdot 2\text{MoO}_3 \cdot 2\text{MoO}_2 \cdot 6\text{H}_2\text{O}$. In this formation only the complex added group, MoO_3 , and not the neutral ammonium molybdate is reduced. Colloidal molybdic acid is rapidly reduced by alcohol to the blue oxide, Mo_3O_8 . Neutral sodium tungstate is only slowly reduced by alcohol in sunlight, so that after a period of five months' exposure to light only a faint blue colour is produced. On the other hand, suspensions of tungstic acid and acidified solutions of tungstates become deep blue in colour when mixed with alcohol and exposed to sunlight for a few hours. The greenish-yellow powder deposited when uranyl chloride dissolved in ether is exposed to sunlight has been examined and found to have the formula UOCl_2 , and the similar precipitate obtained by exposing an aqueous solution of uranyl nitrate containing a little alcohol to sunlight is $\text{UO}_2(\text{NO}_3)_2$.

J. F. S.

The Relation between Uranium and Radium. VII.

FREDERICK SODDY (*Phil. Mag.*, 1919, [vi], 38, 483—488. Compare Soddy and Hitchens, A., 1915, ii, 726).—The subsequent growth of radium in the old uranium preparations, since they were last tested in 1915, has confirmed the earlier result that the growth is proceeding according to the square of the time, and that the product of the two periods of average life of ionium and radium is, to an accuracy of some 5%, 237,500,000 years. Assuming the period of radium to be 2375 years, that of ionium is 100,000 years. It is not to be expected that this period will be determined with much greater accuracy, as the result of subsequent measurements upon these preparations.

F. S.

Electrical Conductivity and Other Properties of Saturated Solutions of Copper Sulphate in the Presence of Sulphuric Acid. H. M. GOODWIN and W. G. HORSH (*Chem. and Met. Eng.*, 1919, 21, 181—182).—The specific electrical conductance at 25° of saturated solutions of copper sulphate contain-

ing sulphuric acid from 0.15 to 3.6 equivalents per litre has been determined, using the customary Wheatstone bridge arrangement with alternating current. The solutions were rotated in a constant temperature bath and the measurements continued until constant, which indicated saturation. The constant of the conductivity cell was determined by measuring the conductivity of normal potassium chloride solution and a solution of sulphuric acid of maximum conductivity. The results, accurate to 0.5%, show that the conductivity increases, following a straight-line law with increasing concentration of sulphuric acid. The solubility of copper sulphate in the presence of sulphuric acid is determined by electro-analysis. The concentration of copper sulphate at the saturation point falls continuously with increase of concentration of sulphuric acid up to 4 equivalents per litre. The acid content of the solutions was determined by titrating with standard sodium hydroxide solution in the presence of copper sulphate, using methyl-orange as an indicator. The density of the solutions was measured by means of a Mohr-Westphal balance. The density first falls with increasing sulphuric acid content and then increases rectilinearly with a minimum at about 0.5 equivalent per litre.

T. H. B.

Applicability of the Precipitated Silver-Silver Chloride Electrode to the Measurement of the Activity of Hydrochloric Acid in Extremely Dilute Solution. G. A. LINHART (*J. Amer. Chem. Soc.*, 1919, **41**, 1175—1180).—Measurements of the *E.M.F.* of cells of the type $\text{Ag, AgCl}|\text{HCl}|\text{H}_2\text{Pt}$ have been carried out for concentrations of hydrochloric acid varying between 0.04826*N* and 0.000136*N*. The cell was made up in a single vessel, consisting of a bulb of about 1200 c.c. capacity fitted with fairly narrow tubes at the top and bottom. The bottom tube contained the silver-silver chloride electrode, and here a current of hydrogen entered just above the electrode; the top tube contained the hydrogen electrode of iridium coated platinum, and above the electrode was an exit tube for the hydrogen. The silver-silver chloride electrode consisted of a layer of fine-grained electrolytic silver covered with a layer of precipitated silver chloride. After filling, the cell was placed in a thermostat and kept at a temperature of $25^\circ \pm 0.01^\circ$ for three to four days to come to equilibrium, and then the *E.M.F.* measurements were made over a considerable period of time until constant values were obtained. The following values of the *E.M.F.* for a hydrogen pressure of 1 atm. are obtained: HCl , 0.04826*N*, 0.3874 volt; 0.00965*N*, 0.4658 volt; 0.004826*N*, 0.5002 volt; 0.001000*N*, 0.5791 volt; 0.000483*N*, 0.6161 volt; 0.000242*N*, 0.6514 volt; and 0.000136*N*, 0.6805 volt. The *E.M.F.* is calculated to molecular concentration of hydrogen and chloride ions on the assumption of complete ionisation; these values extrapolated at infinite dilution yield the value 0.2234 volt, from which the degree of dissociation is calculated for each dilution.

J. F. S.

Transport Number of Chromic Ions in Violet Chloride Solutions. KARL HOPFGARTNER (*Monatsh.*, 1919, **40**, 259—269).—The transport number of the chromic ion in hydrochloric acid solu-

tions of violet chromic chloride has been determined by the Hittorf method. The determinations were effected with solutions of three concentrations (1.00, 0.32, and 0.075 equivalent). The transport numbers found were 0.318 ± 0.005 , 0.357 ± 0.003 , and 0.414 ± 0.005 respectively, which extrapolate to the value 0.446 for the concentration zero, and lineally extrapolate to 0.430. From these values the mobility of the chromic ion is estimated by various methods as 53, 49.5, and 46.3, and of these the first value is probably too high. The results indicate that the chromic ion is surrounded by a fairly large water sheath, although the various methods of calculating the magnitude of this give results which vary considerably.

J. F. S.

Anodic Peroxidation of Manganese in an Acid Medium in Presence of Silver Salts.

ARMANDO RUSCONI (*Arch. farm. sper. sci. aff.*, 1919, **27**, 94—96).—When 30% sulphuric acid containing a small proportion (0.05%) of manganous sulphate is electrolysed in a U-shaped voltameter with a potential difference of 5—6 volts, the formation of traces of permanganic acid at the anode is observable after a few minutes. If, however, the solution contains also a few drops of saturated silver sulphate solution, the formation of permanganic acid at the anode is immediate and rapid. Similar results are obtained if the sulphuric acid is replaced by concentrated sodium hydrogen sulphate solution (compare Marshall, A., 1901, ii, 156; Scagliarini and Casali, A., 1913, ii, 181).

T. H. P.

Flowing Metal Vapour Arcs. EMIL PODSZUS (*Zeitsch. Elektrochem.*, 1917, **23**, 179—181).—A metallic vapour arc is described which will burn steadily and continuously in any atmosphere. The lamp consists of a large globe of glass or quartz open at the bottom and fitted with a narrow exit tube at the top. The wide opening at the bottom stands in an iron dish containing mercury, and through the bottom of which are three openings. A narrow glass tube for admitting gas passes through the first; the second opening admits the cathode vessel, and the third the anode vessel. The cathode vessel is made of iron, and down the middle of it a tube of boron nitride passes; covering the top of the cathode is a plate of tungsten perforated by a narrow opening in the centre. The object of the boron nitride tube and the tungsten plate is to stabilise the arc and to prevent fluctuations of the mercury or amalgam which constitutes the cathode. The anode is a tungsten rod. The arc is struck by lowering the anode until it touches the cathode and then drawing it away. The arc produced is a thin, quiet flame, which is affected in colour by the gases in the globe and by the metal used as cathode. In hydrogen the light is greenish-white; in nitrogen bluish-white. All compound gases introduced into the arc were reduced; thus the solid element was obtained from boron trichloride and titanium tetrachloride, whilst calomel was also produced.

J. F. S.

A New Method for the Rapid Determination of Critical Temperatures. Application to Carbonyl Chloride. L. HACKSPILL and MATHIEU (*Bull. Soc. chim.*, 1919, **25**, 482—485).

—A simple apparatus for the determination of critical temperatures consists of a cylinder of aluminium or copper about 25 cm. long and 5 cm. in diameter wound throughout its entire length with nickel wire, by which it is heated electrically. The liquid to be examined, contained in a thick glass tube, is placed in a hole in the axis of the cylinder, and can be viewed through a longitudinal slit in the cylinder. A second hole parallel to the first is provided for a thermometer. The critical temperature of carbonyl chloride was found to be $183 \pm 0.5^\circ$ with this apparatus.

E. H. R.

The Critical Temperature as a Single Function of the Surface Tension. II. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1919, **17**, 325—328. Compare this vol., ii. 183). The author deduces, on theoretical grounds, the equation, previously put forward (*loc. cit.*), connecting the surface tension with the critical temperature. The relationship is verified in the case of a number of organic liquids.

J. F. S.

The Equation of State of Ethyl Formate. E. ARIÈS (*Compt. rend.*, 1919, **169**, 602—605).—The equation of state of ethyl formate, like that of ethyl acetate (compare this vol., ii, 360), satisfactorily represents the thermal properties of this fluid, except in so far as concerns the heat of vaporisation and the density of the vapour over a temperature range extending from the critical temperature to 35° below it.

W. G.

Standardisation of the Sulphur Boiling Point. E. F. MUELLER and H. A. BURGESS (*J. Amer. Chem. Soc.*, 1919, **41**, 745—763).—The boiling point of sulphur as a standard temperature has been investigated and the conditions under which it should be determined examined. The suggestion that the reflecting power of the inner surface of a radiation shield may influence the temperature assumed by a resistance thermometer is confirmed. A number of shields, both of glass and porcelain, have been examined, and several satisfactory forms are described. The influence of the type of boiling apparatus on the observed temperature is found to be very small. The presence of 0.05% of arsenic in the sulphur has no effect on the boiling point, but 0.10% raises the boiling point 0.02° , 0.05% of selenium, together with 0.10% of arsenic, raises the boiling point 0.08° , and 0.10% of arsenic and 0.10% of selenium raises the boiling point 0.09° . The boiling point of pure sulphur at 760 mm. pressure is 421.73° . The vapour pressure over the range 700 mm. to 800 mm. has been redetermined, and from these values an equation for calculating the boiling point at various pressures is deduced. This has the form $t = 444.60 + 0.0910(p - 760) - 0.000049(p - 760)^2$. A résumé of the conditions to be observed in determining the boiling point of sulphur for standardisation purposes is appended to the paper.

J. F. S.

Determination of Boiling Points of Solutions. F. G. COTTRELL (*J. Amer. Chem. Soc.*, 1919, **41**, 721—729).—A modified boiling-point apparatus is described for solutions whereby the conditions obtaining in the determination of the boiling point of pure liquids are imitated. In the present method, the Beckmann thermometer is placed in the vapour phase and the bulb coated with a thin film of the boiling liquid. The coating of the bulb with the boiling solution is effected by means of a narrow glass tube, which is placed in the liquid; this tube is funnel-shaped at the bottom and sealed at the top, but with a lateral hole just above the bulb of the thermometer. When the liquid boils, bubbles of vapour pass up the tube and carry boiling liquid into a cup through a loosely fitting opening in which the stem of the thermometer passes, the liquid flows over the bulb, and slowly drips back into the solution. It is claimed that this arrangement entirely removes errors due to superheating and yields accurate results extremely readily.

J. F. S.

Laws of Concentrated Solutions. VI. The General Boiling-point Law. EDWARD W. WASHEURN and JOHN W. READ (*J. Amer. Chem. Soc.*, 1919, **41**, 729—741).—The boiling points of concentrated solutions of naphthalene and diphenyl in benzene have been determined by means of the Cottrell boiling-point apparatus (preceding abstract). In the determinations, two pieces of apparatus were used, in one of which the pure solvent was kept continually boiling, and in the other the solution, so that the elevation of the boiling point was read directly and was independent of slight pressure changes. The apparatus was further modified by the addition of a side-tube, from which quantities of the solution were extracted for analysis. In the present case, the analysis consisted in determining the density of the solution at 25° and calculating the composition by means of an empirical equation connecting density and composition. The boiling-point law for ideal solutions and the connexion between the boiling-point elevation and the barometric pressure are considered. It is also shown how the molecular weight of a dissolved substance which undergoes solvation may be calculated from the elevation of the boiling point.

J. F. S.

Molecular-weight Determination by Direct Measurement of the Lowering of the Vapour Pressure of Solutions. ROBERT WRIGHT (T., 1919, 115, 1165—1168).

The Evaporation of Concentrated and Saturated Solutions of Ammonium Nitrate, Vapour Pressures, Heats of Solution, and Hydrolysis. E. B. R. PRIDEAUX and R. M. CAVEN (*J. Soc. Chem. Ind.*, 1919, **38**, 353—355r).—The vapour pressures of 47·8%, 60·4%, and saturated solutions of ammonium nitrate have been measured between 40° and 100°. In 60·4% solutions, which are about saturated at the ordinary temperature, the pressure still rises rapidly with rise of temperature, but the

pressures of saturated solutions are low, being no more than 17 cm. at 100°. The heats of evaporation, calculated from the vapour pressures, are, in the case of unsaturated solutions, about 50 cal. lower than that of water at the same temperature, and appear to reach a maximum at some temperature between 60° and 70°. The maximum is more pronounced with saturated solutions, occurring at about 60° with a latent heat of 400 to 450 cal.

When ammonium nitrate solutions are evaporated in contact with iron, there is considerable loss of ammonia and corrosion of the iron by the hydrolytic nitric acid. In acid-resisting vessels or vessels of aluminium, the loss of ammonia through hydrolysis is almost entirely obviated.

E. H. R.

Improved Apparatus for the Estimation of Vapour Pressures. ALLAN MORTON (*J. Soc. Chem. Ind.*, 1919, 38, 363—364r).—Difficulties having arisen in the determination of the vapour pressures of certain organic liquids on account of the solvent action of these liquids on the lubricants employed for the stopcocks, an apparatus was devised in which taps were entirely avoided. The apparatus took the form of a U-shaped barometer with a bottom mercury reservoir. To the top of each barometer tube was fused a capillary tube, which was bent downwards with its end dipping into a mercury cup. The mercury having been thoroughly cleaned and dried, a sample of the liquid of which the vapour pressure was to be determined was placed in one of the two mercury cups, and, by suitable manipulation of the bottom reservoir, drawn up into one of the arms of the barometer. The difference between the mercury levels in the two arms was a measure, of course, of the vapour pressure.

E. H. R.

The Vapour Pressures of Mixtures of Ether and Sulphuric Acid. ALFRED W. PORTER (*Trans. Faraday Soc.*, 1919, 14, 280).—A correction to some remarks made by the author in a discussion on a paper by F. H. Campbell (*A.*, 1916, ii, 83).

E. H. R.

Use of Coal as a Substitute for Talcum to Induce Rapid Boiling. E. C. KENDALL (*J. Amer. Chem. Soc.*, 1919, 41, 1189—1190).—Small, compact pieces of anthracite serve excellently for bringing about rapid boiling of liquids and solutions, and also for preventing the bumping in Kjeldahl flasks. Powdered anthracite has not the same action, and anthracite which has been kept in water for some time loses its efficacy, but after baking for some time the efficacy is regained.

J. F. S.

The Occlusion of Gases by Metals. Introductory Address to General Discussion. SIR ROBERT HADFIELD (*Trans. Faraday Soc.*, 1919, 14, 173—191).—A historical account of the subject, with special reference to the effect of occluded gases in steel castings. A bibliography is appended.

E. H. R.

General Remarks on Occlusion of Gases in Metals.

ALFRED W. PORTER (*Trans. Faraday Soc.*, 1919, 14, 192-197).—The term "occlusion" probably covers a number of different phenomena which may take place either singly or in conjunction. These can be enumerated under six heads: first, chemical combination of gas with metal, for example, hydrogen with sodium, potassium, or palladium; secondly, simple solid solution, either separately or in conjunction with the first; thirdly, solid solution in contiguous phases; fourthly, solution accompanied by surface adsorption; fifthly, surface condensation under molecular forces, unaccompanied by solution; sixthly, inclusion, as when large or minute bubbles become entangled in the molten, viscous mass. The work of earlier investigators on occlusion, particularly the occlusion of hydrogen by palladium, is discussed from the point of view of this classification of the phenomena. The influence of condensed gases on the Volta effect is also discussed. E. H. R.

The Physical Properties of Metals as Affected by their Occluded Gases.

COSMO JOHNS (*Trans. Faraday Soc.*, 1919, 14, 198-201).—To explain the profound effect of occluded gases on the physical properties of metals, for instance, the rendering brittle of iron or copper by hydrogen, the following theory is proposed. As a working hypothesis, it is assumed that hydrogen is soluble in the molten metals, but insoluble in the solid, and the theory is adopted that the tenacity of solid metals and the strength of the crystal boundaries are due to the presence of amorphous material, that is, an under-cooled liquid, which serves to cement the crystal grains which compose the solid mass. This intercrystalline matter must contain more hydrogen in solution than the solid metal can hold, and it is therefore at the crystal boundaries that the change in properties occurs, and the brittleness of the whole mass is explained. Relatively small quantities of gas dissolved in the intercrystalline material might thus cause profound changes in the properties of the metal.

The carbon monoxide and carbon dioxide found occluded in steel are probably formed by interaction of dissolved oxide of iron and carbon at the particular temperature when iron oxide, being thrown out of solution as freezing progresses, becomes concentrated in the mother liquor between the growing crystals and reacts with the carbon which has not suffered the same concentration. The gases would thus become concentrated in the intercrystalline layers, and would have the same effect as the hydrogen in copper and iron. Such data as are available on the physical properties of metals or alloys all refer to metals containing unknown quantities of occluded gases, which may profoundly modify their properties, and consequently knowledge of the properties of pure metals, if such can be obtained, is lacking. E. H. R.

Theories of Occlusion: the Sorption of Iodine by Carbon.

J. W. McBAIN (*Trans. Faraday Soc.*, 1919, 14, 202-212).—The term "sorption" is employed to include the phenomena of adsorp-

tion, absorption or true solid solution, and chemical reaction, all of which may accompany the fixation of a gas by a solid, and the occlusion of gases by metals is considered as a special instance of the process of sorption. The three processes involved in the phenomenon of sorption differ widely in their time relationships. True adsorption is nearly instantaneous, whilst absorption should obey Fick's diffusion law, commencing with a very high velocity for the first few moments and rapidly falling off with time. Chemical reaction may show the most varied time relationships, since it often proceeds vigorously in surface films as well as in solid solution. Since the occlusion of gases is hastened by rise of temperature, it is reasonable to conclude that the phenomena involved are largely those of diffusion, that is, of absorption rather than adsorption, whilst chemical reaction may play a prominent part.

It was shown by Davis (T., 1907, **91**, 1666) that the sorption by carbon of iodine dissolved in benzene, toluene, and other solvents consists of a surface condensation and a diffusion into the interior. The surface condensation is nearly instantaneous, whilst the diffusion proceeds for weeks or months. After an interval of eleven years, the experiments set up by Davis have been re-examined, and the sorption due to the slow diffusion of the iodine into the charcoal is found to be still continuing. Fresh experiments extending over four years have also confirmed Davis's results.

E. H. R.

Balanced Reactions in Steel Manufacture. ANDREW McCANCE (*Trans. Faraday Soc.*, 1919, **14**, 213—223).—A discussion of the equilibrium conditions in the open-hearth furnace during the manufacture of steel. The distribution of ferrous oxide between the steel and the slag and the influence of the furnace gases are particularly considered.

E. H. R.

A Few Suggestions on the Theories of Occlusion of Gases by Metals. J. H. ANDREW (*Trans. Faraday Soc.*, 1919, **14**, 232—239).—From a consideration of the experimental evidence available, it is concluded that the occlusion of hydrogen by palladium is dependent on the presence of the active, amorphous form of the metal. Palladium in the crystalline state, free from contamination by the amorphous phase, is inactive towards hydrogen in the cold, but can be rendered active by continually pumping in and extracting gas from the metal, this treatment giving rise to the amorphous form. An amorphous layer of the metal will act as a vehicle for conveying the gas into the crystalline metal, the adsorbed layer of gas acting as a layer of extreme concentration and exerting the same effect as a high external pressure. In the occlusion of hydrogen by iron, the amorphous phase, in this case the intercrystalline cement, probably plays a prominent part. For instance, when a piece of wrought iron is immersed for some time in a saturated solution of sodium hydroxide at 100°, the mass becomes brittle, because the gas is absorbed

more rapidly in the amorphous intercrystalline layers than by the crystals themselves, and the expansion of these layers forces the crystals apart and weakens their cohesion. After remaining longer in the sodium hydroxide, the iron loses its brittleness, because the hydrogen gradually diffuses into the crystals from the intercrystalline cement. Electrolytic iron, being already saturated with hydrogen, is unaffected by sodium hydroxide. It is concluded that diffusion and occlusion are more or less identical, and can be explained by simple physical laws without reference to chemical combination.

E. H. R.

Solutions. A. REYCHLER (*J. Chim. Phys.*, 1919, **17**, 209—265).—A theoretical paper in which many of the properties of solutions are considered. On the basis of Perrin's value of N , the Avogadro number, it is calculated that the mean kinetic energy of one molecule at 0° is 0.5×10^{-13} ergs, and that the charge e of one electron is 4.2×10^{-10} electrostatic units. An explanation of the mechanism of osmotic pressure is evolved, and a method of interpreting certain anomalies observed in osmotic pressure values is indicated. The author has developed the formulæ for calculating molecular weights from boiling-point elevations and freezing-point depressions on the basis of the vapour pressure formula. The nature of ionisation is considered, and it is shown that the ionic equilibrium is a condition of balance between the disruptive forces of the water and the attractions of the ions for one another, which, being of an electrical character, are never entirely eliminated, since they can act over a distance. A connexion is established between ionisation and an adsorption phenomenon. The reasons for the variation of the index in the dissociation laws of Storch and Noyes are considered.

J. F. S.

Unique Case of a Liquid that Exhibits a Minimum Solubility in an Unstable Region. MARSTON TAYLOR BOGERT and JACOB EHRLICH (*J. Amer. Chem. Soc.*, 1919, **41**, 741—745).—On cooling a clear solution of the monohydrate of 3:5-dimethoxyacetophenetidide in boiling water, there appeared a cloud of minute drops, which disappeared on further cooling, with the formation of a clear solution; from this, on continued cooling, white crystals eventually separated. To ascertain the nature of this behaviour, the solubility of this compound has been determined over the temperature range 21.8 — 173.6° . It is shown that the solubility increases with rise of temperature up to 87.5° , when the solid in contact with the solution melts. The solubility of the liquid hydrate increases more rapidly with further rise of temperature. Below 87.5° , the solubility of the liquid hydrate decreases with falling temperature until a point somewhere between 68.5° and 58.1° is reached, when it again increases. Hence the liquid hydrate has a minimum solubility at about 63° . The following solubilities in molecular percentages are recorded. (1) The solid hydrate: 21.8° , 0.010; 39.4° , 0.020; 57.0° , 0.046; 69.5° , 0.076; 72.8° , 0.091; 77.1° , 0.120; 80.2° , 0.151; 84.2° , 0.203; 86.6° , 0.237;

86.9°, 0.257. (2) The liquid hydrate: 35.6°, 0.301; 45.6°, 0.257; 58.1°, 0.237; 68.5°, 0.237; 84.3°, 0.257; 99.8°, 0.303; 111.1°, 0.361; 118.4°, 0.407; 129.2°, 0.499; 173.6°, 2.041. J. F. S.

Intermediate and Complex Ions. V. The Solubility Product and Activity of the Ions in Bivalent Salts. WILLIAM D. HARKINS and H. M. PAINE (*J. Amer. Chem. Soc.*, 1919, 41, 1155—1168. Compare A., 1917, ii, 77).—In previous papers (*loc. cit.*) it is shown that salts of tri-ionic and higher types ionise in steps and give, even in 0.1*N*-solutions, a large number of intermediate ions. In the present paper, the ionisation of salts composed of a bivalent cation and anion are considered. For this purpose, the solubility of calcium sulphate in water, and in solutions of copper sulphate, magnesium sulphate, and potassium nitrate, has been determined at 18° and 25°. The equivalent conductivity of various concentrations of the four salts and of the solutions of calcium sulphate in the others has been determined at the same temperatures, as well as the densities. The results show that the solubility relations of calcium sulphate when common ions are added are very similar to those of the higher type salts. This indicates the probability that complex ions, such as $\text{Ca}(\text{SO}_4)_2$ and Ca_2SO_4 , are present in the solutions. These complex ions differ from what are usually considered under this title, since they are present to a considerable extent in dilute solutions, so in this sense they are more like intermediate ions. If it is assumed that such complex ions are absent, the solubility product, calculated on this basis, is found to increase with great rapidity as the concentration increases; thus, if the total ion concentration increases from 0.02*N* to 0.10*N*, the solubility product is trebled, so, if only simple ions are present, this activity decreases very rapidly with an increase in concentration. On the other hand, the solubility found for the un-ionised part, on the basis of this assumption, remains much more constant than in the case of uni-univalent salts. The change in the slope of these curves is in the direction which is to be expected if complex ions are present. The percentage concentration of such complexes is much higher in copper sulphate solutions than in magnesium sulphate solutions at the lower concentrations. J. F. S.

Reciprocal Solubility of Mixtures of Water, Alcohol, and Ether. A. BOUTIN and A. SANFOURCHE (*Bull. Soc. chim.*, 1919, [iv], 25, 458—463).—The solubility of water in ether varies but little with temperature, but that of ether in water falls from 12.2% at -3.3°, the freezing point of water saturated with ether, to 4.0% at 35°. By adding one constituent to mixtures of the other two of known composition at 15° until two layers were just formed or just disappeared, limiting values were obtained for a series of ternary mixtures of varying composition. The results are conveniently plotted on a triangular diagram, each corner representing 100% of one constituent. A curve is obtained dividing the triangle into two zones, the one representing homogeneous and the other

heterogeneous mixtures. By drawing tangents to the curve from the points representing pure ether and pure water, the homogeneous zone is divided into six areas. One of these represents mixtures which cannot be made heterogeneous by addition of one constituent; two represent those which can only be made heterogeneous by addition of ether; two others represent those which can only be made heterogeneous by addition of water; whilst the last area represents mixtures which can be separated into two layers by either water or ether. No homogeneous mixture can be made heterogeneous by addition of alcohol alone. E. H. R.

Crystal Lattices and Bohr's Atom Model. L. VEGARD (*Ber. deut. physikal. Ges.*, 1919, **21**, 383—385).—A short criticism of a paper by Born and Landé (this vol., ii, 188), in which the author states that some of the views expressed in the paper, and others attributed to Sommerfeld (A., 1918, ii, 303) were in reality put forward by him at an earlier date (A., 1918, ii, 93, 94, 144), and in consequence he claims priority. J. F. S.

Crystal Lattices and Bohr's Atom Model. M. BORN and A. LANDÉ (*Ber. deut. physikal. Ges.*, 1918, **21**, 385—387. Compare preceding abstract).—An answer to Vegard's criticism (*loc. cit.*), in which the authors allow the priority claim in some respects, but maintain their own in others. J. F. S.

An Experiment Relating to Atomic Orientation. T. R. MERTON (*Phil. Mag.*, 1919, [vi], **38**, 463—464).—On the two assumptions, first, that the axes at right angles to the planes of the rings of electrons in the atom are orientated in a regular manner in a crystal structure, and, secondly, that the direction of expulsion of α - and β -particles from a radioactive atom is also related in some regular manner to this atomic axis, there should be a difference in the α - and β -activities of different faces of certain crystals of radioactive substances. The α -activities of three different faces of large crystals of uranium nitrate have been tested and found to be the same within the error of measurement, so showing that at least one of the two assumptions is incorrect. It is considered the more probable that the α -rays are shot out of the nucleus without regard to the orientation of the atomic axis. F. S.

Colloid Chemistry and its General and Industrial Applications. Second Report. F. G. DONNAN, W. C. M. LEWIS, E. F. ARMSTRONG, ADRIAN J. BROWN, C. H. DESCH, E. HATSCHEK, H. R. PROCTER, W. RAMSDEN, A. S. SHORTER, H. P. STEVENS, and H. B. STOCKS (*Rep. Brit. Assoc.*, 1918, 1—172).—The present report consists of articles on the following subjects: (i) Peptisation and precipitation (pp. 15), Wilder D. Bancroft; (ii) Emulsions (pp. 5), E. Hatschek; (iii) The Liesegang phenomenon (pp. 5), E. Hatschek; (iv) Electrical endosmose, I. (pp. 14), T. R. Briggs; (v) Electrical endosmose, II. (pp. 14), T. R. Briggs: this article deals with de-watering of peat and clay, electrical tanning, preservation of

timber, manufacture of bricks and electro-therapeutics; (vi) Colloid chemistry in the textile industries (pp. 18), W. Harrison; (vii) Colloids in agricultural phenomena (pp. 12), E. J. Russell; (viii) Sewage purification (pp. 15), E. Arden; (ix) Colloid problems in dairy chemistry (pp. 22), W. Clayton; (x) Colloid chemistry in physiology (pp. 38), W. M. Bayliss; (xi) Administration of colloids in disease (pp. 18), A. B. Searle. J. F. S.

Vibration and Syneresis of Silicic Acid Gels. HARRY N. HOLMES, WILFORD E. KAUFMANN, and HENRY O. NICHOLAS (*J. Amer. Chem. Soc.*, 1919, **41**, 1329—1336).—The tones produced by vibrating silicic acid gels have been investigated. Silicic acid gels were made which on tapping in thin-walled glass tubes produced a tone two octaves above middle *C*. Such gels vibrate as rigid solids, but tension is an important factor. That the gels are under considerable tension is shown by their great contraction in vaselined tubes. Contracted gels removed from vaselined tubes have a lower vibration frequency than similar gels adhering to the walls of tubes of equal diameter. Since vibration frequency varies inversely as the diameter of the gel column, tension must exert some influence on pitch. Vibration frequency varies directly as the concentration of silicic acid, increases with excess of mineral acid, and decreases with excess of organic acids. Syneresis (separation of aqueous solutions from highly hydrated gels) increases with increase in concentration of silicic acid, increases with excess of mineral acids, and decreases with excess of organic acids. For acid gels the factors which increase vibration frequency also increase syneresis. Vibration and syneresis are directly related to tension, but basic gels are abnormal in this respect. Syneresis varies directly as the free surface. When gels contract in vaselined tubes far more liquid separates than from equal volumes of gel in plain tubes to which the gel adheres. J. F. S.

Influence of the Age of Ferric Arsenate on its Peptisation. HARRY N. HOLMES and PAUL H. FALL (*J. Amer. Chem. Soc.*, 1919, **41**, 713—717).—Determinations have been made of the amount of a 5*N*-solution of ferric chloride solution required to peptise 1.32 grams of ferric arsenate of various ages. The arsenate was prepared in bottles by adding 3 c.c. of 5*N*-ferric chloride solution to 17.6 c.c. of *M*/5-disodium arsenate solution and shaking vigorously for three minutes. The samples were then preserved, and after measured intervals were treated with ferric chloride solution and vigorously shaken until, by the trial method, the minimum quantity of ferric chloride required for peptisation was found. The experiments were made with ferric arsenate of ages varying up to fifty-six days. It is shown that the amount of ferric chloride required increases rapidly if the precipitate is allowed to age before peptisation—up to an age of one or two days. After this there is only a very small increase in the amount of ferric chloride needed even if the precipitate is kept a month before peptisation. The explanation of this behaviour is found in a decrease in hydration

of the precipitate—rapid during the first day and slow afterwards; also in the formation of larger aggregates with a consequent decrease in the external surface of the particles. Both influences retard diffusion of a solution of a peptising agent and greatly check the rate of peptisation. A few experiments, using ammonium hydroxide and sodium hydroxide as peptising agent, led to similar results.

J. F. S.

Jellies [formed] by Slow Neutralisation. HARRY N. HOLMES and PAUL H. FALL (*J. Amer. Chem. Soc.*, 1919, **41**, 763—764).—Clear gels of ferric arsenate, peptised by ferric chloride, can be prepared by entirely filling a bottle with the sol, covering the neck with a piece of gold-beaters' skin, and placing in a tube attached to the neck 2 c.c. of *N*-ammonium hydroxide, 2 c.c. of saturated calcium hydroxide solution, or 2 c.c. of sodium acetate solution. The base diffuses through the membrane and neutralises the free acid slowly enough to allow of the formation of a perfect gel structure.

J. F. S.

Calculation of the Equilibrium Constants in the Deacon Process. W. D. TREADWELL (*Zeitsch. Elektrochem.*, 1917, **23**, 177—179).—A theoretical paper, in which, making use of known data and the dissociation constants of water and hydrogen chloride, the author shows that the equilibrium constants of the Deacon process are given by the expression $\log K_p = 6034/T - 6.972$. This expression is trustworthy between 300° and 1800°, and the values are nearly correct at temperatures in the region of the atmospheric temperature.

J. F. S.

Influence of Substitution in the Components on the Equilibrium of Binary Solutions. VII. Binary Solutions Equilibria of α - and β -Naphthylamine respectively with Nitro-derivatives of Benzene. ROBERT KREMAN and GEORG GRASSER (*Monatsh.*, 1916, **37**, 723—753. Compare this vol., ii, 275).—Fusion curves have been produced for the binary systems formed between α - and β -naphthylamine respectively and the three dinitrobenzenes, 2:4-dinitrotoluene, 1:3:5-trinitrobenzene, the three mononitrophenols, and 2:4-dinitrophenol respectively. It is shown that neither α - nor β -naphthylamine forms compounds with *o*-dinitrobenzene or *o*-nitrophenol; β -naphthylamine forms no compounds with 2:4-dinitrotoluene. Equimolecular compounds are formed between α -naphthylamine and *p*-dinitrobenzene (m. p. 81.8°), *m*-dinitrobenzene (m. p. 63.8°), 2:4-dinitrotoluene (m. p. 62°), *m*-nitrophenol (m. p. 56.3°), *p*-nitrophenol (m. p. 68.2°), and 2:4-dinitrophenol (m. p. 104.5°). A compound of unknown and undetermined composition is indicated in the system α -naphthylamine-trinitrobenzene. Equimolecular compounds are formed between β -naphthylamine and *p*-dinitrobenzene (m. p. 91°), *m*-dinitrobenzene (m. p. 53.3°), 1:3:5-trinitrobenzene (m. p. 161°), *m*-nitrophenol (m. p. 63.5°), *p*-nitrophenol (m. p. 81.5°), and 2:4-dinitrophenol (m. p. 72.3°). In the case of the

compounds with the dinitrobenzenes, the range of existence is greater for the compounds with α -naphthylamine than for those with β -naphthylamine.

J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. VIII. ROBERT KREMANN and WILHELM CSANYI (*Monatsh.*, 1916, **37**, 755—760. Compare preceding abstract).—Fusion curves have been produced for the binary systems formed between β -naphthylamine and the three dihydroxybenzenes. It is shown that β -naphthylamine forms equimolecular compounds with resorcinol (m. p. 77.6°) and catechol (m. p. 81.3°). A compound (m. p. 141.7°) is formed between two molecules of β -naphthylamine and one molecule of quinol.

J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. IX. A Comparative Determination of the Degree of Dissociation of some Additive Compounds in the Molten Condition. ROBERT KREMANN and GEORG GRASSER (*Monatsh.*, 1916, **37**, 761—774. Compare preceding abstracts).—The degree of dissociation of the equimolecular compounds, formed by naphthalene, α -naphthylamine, β -naphthylamine, and aniline with various other substances, has been calculated. The calculation was carried out by means of the formula of van Laar, $\alpha_0 = (RT_0^2/Q_0)[x^2(1+x)]/[4(T_0-T)]$, in which T_0 is the melting point of the pure compound, α_0 the degree of dissociation, T is the melting point of a mixture of the compound and its components in a concentration x , and Q_0 is the total heat of fusion which is made up of the real heat of fusion q_0 and the heat of dissociation λ . Q_0 is determined experimentally from the initial direction of the fusion curve of the compound and an indifferent substance by means of the expression $(dT/dx) = -RT_0^2/(q_0 + \alpha\lambda) = -RT_0^2/Q_0$. As indifferent substances, p -nitrotoluene and nitrobenzene were used in the experiments. The following values of α_0 were obtained: naphthalene- m -dinitrobenzene, 0.93; naphthalene- p -dinitrobenzene, 0.87; naphthalene-2:4-dinitrotoluene, 0.86; naphthalene-2:4-dinitrophenol, 0.83; α -naphthylamine- m -dinitrobenzene, 0.53; α -naphthylamine-2:4-dinitrotoluene, 0.58; α -naphthylamine- m -nitrophenol, 0.55; α -naphthylamine- p -nitrophenol, 0.56; α -naphthylamine-2:4-dinitrophenol, 0.28; β -naphthylamine- m -dinitrobenzene, 0.88; β -naphthylamine- m -nitrophenol, 0.55; β -naphthylamine- p -nitrophenol, 0.54; β -naphthylamine-2:4-dinitrotoluene, 0.61; aniline- m -dinitrobenzene, 0.23; aniline-2:4-dinitrotoluene, 0.67; aniline-phenol, 0.44; and aniline- m -cresol, 0.10.

J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XIX. The Binary Systems of Antipyrine with Phenols and their Derivatives. ROBERT KREMANN and OTFRIED HAAS (*Monatsh.*, 1919, **40**, 155—188. Compare this vol., ii, 275).—By means of melting-point curves, the binary systems, antipyrine and phenolic sub-

stances, have been investigated with the object, as in the previous communications, of ascertaining the influence of substitution on the tendency of organic substances to form molecular compounds. In the present papers, the systems antipyrine with phenol, salicylic acid, α -naphthol, β -naphthol, *o*-nitrophenol, *p*-nitrophenol, *m*-nitrophenol, 2:4-dinitrophenol, pyrogallol, catechol, quinol, and resorcinol have been examined and the fusion curves constructed. It is shown that an equimolecular compound is formed between antipyrine and salicylic acid, phenol, α -naphthol, and β -naphthol respectively. In the case of the nitrophenols, antipyrine, as in other cases, forms no compounds with *o*-nitrophenol, but with *p*-nitrophenol three molecular compounds are formed, namely, two molecules of antipyrine with one molecule of *p*-nitrophenol, and one molecule of antipyrine with one and two molecules, respectively, of *p*-nitrophenol. In the cases of *m*-nitrophenol, pyrogallol, and 2:4-dinitrophenol, only the melting-point curves of the pure components could be observed, owing to the extreme slowness of the crystallisation of the melt lying between them. There is little doubt that in these cases one or more molecular compounds exist, but they could not be obtained. Catechol forms three molecular compounds with antipyrine, one molecule of the phenol to one and two molecules of antipyrine respectively, and two molecules of the phenol to one molecule of antipyrine. In the case of quinol, two compounds are formed, two molecules of antipyrine to one and three molecules, respectively, of quinol. J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XX. The Binary Systems of Acenaphthene with some Nitro-derivatives of Benzene. ROBERT KREMANN and OTFRIED HAAS (*Monatsh.*, 1919, 40, 189—204. Compare preceding abstract).—Fusion curves have been constructed for the binary systems formed between acenaphthene and the three dinitrobenzenes, 2:4-dinitrotoluene, the three nitrophenols, 2:4-dinitrophenol, and picric acid respectively. The systems acenaphthene-*o*-dinitrobenzene and acenaphthene-*p*-dinitrobenzene form no compounds, but simple eutectics; *m*-dinitrobenzene, on the other hand, forms an equimolecular compound (m. p. 70.1°). In the case of dinitrotoluene, an equimolecular compound is also formed (m. p. 57.5°). No compounds are formed between acenaphthene and the three nitrophenols, simple eutectics being formed in each case. An equimolecular compound is formed between 2:4-dinitrophenol and acenaphthene (m. p. 86°), and a similar equimolecular compound is formed between picric acid and acenaphthene (m. p. 151.5°). J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXI. The Binary Systems of Trimethylcarbinol with Phenols and Amines respectively. ROBERT KREMANN and OTTO WLK (*Monatsh.*, 1919, 40, 205—236. Compare preceding abstract).—Fusion curves have

been constructed for the binary systems trimethylcarbinol and the three dihydroxybenzenes, α -naphthol, β -naphthol, pyrogallol, *p*-toluidine, the three phenylenediamines, α -naphthylamine and β -naphthylamine respectively. It is shown that two compounds are formed between catechol and trimethylcarbinol, namely, between two molecules of catechol and one molecule of the alcohol (m. p. 69.7°), and between two molecules of the alcohol and one molecule of catechol (m. p. 29°). In the case of resorcinol and trimethylcarbinol, two compounds are also formed, an equimolecular compound (m. p. 45.8°) and a compound between two molecules of the alcohol and one molecule of resorcinol (m. p. 47.3°). The volatility of trimethylcarbinol rendered the examination of the fusion curve with quinol incomplete, so that nothing can be said of any compounds which may be formed in this case. Pyrogallol, α -naphthol, and β -naphthol each form a single compound with trimethylcarbinol which melt at 56.2° , 1.0° , and 24° respectively. Trimethylcarbinol forms no compounds, but only simple eutectics with *p*-toluidine, *m*-phenylenediamine, and *p*-phenylenediamine. Two compounds are formed between trimethylcarbinol and β -naphthylamine, namely, a compound between two molecules of the amine and one molecule of the alcohol (m. p. 95.5°), and between one molecule of the amine and two molecules of the alcohol (m. p. 92°). In the case of α -naphthylamine, three compounds are formed, namely, between two molecules of the amine and one molecule of the alcohol (m. p. 29.5°), one molecule of the amine and two molecules of the alcohol (m. p. 24.1°), and between one molecule of the amine and six molecules of the alcohol (m. p. 16.0°).

J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXII. The Binary Systems Triphenylcarbinol with Phenols and Amines respectively. ROBERT KREMANN and OTTO WLK (*Monatsh.*, 1919, **40**, 237—258. Compare preceding abstracts).—Fusion curves have been constructed for the binary systems triphenylcarbinol and phenol, α -naphthol, β -naphthol, quinol, catechol, resorcinol, *p*-toluidine, α -naphthylamine, and β -naphthylamine respectively. It is shown that phenol, α -naphthol, and β -naphthol form only simple eutectics, and no compounds with triphenylcarbinol. Triphenylcarbinol forms a single compound with two molecules of catechol (m. p. 82.0°) and with two molecules of quinol (m. p. 151.6°). In the case of resorcinol, a reddish-brown substance of high melting point separates from the mixture when the concentration of the mixture lies between 25% and 55% of triphenylcarbinol. This compound has not been further examined and is not a molecular compound. No molecular compounds are formed between triphenylcarbinol and *p*-toluidine, α -naphthylamine and β -naphthylamine, respectively, simple eutectics being formed in each case.

J. F. S.

Interchange of Bases in Permutite. GERTRUD KORNFIELD (*Zeitsch. Elektrochem.*, 1917, **23**, 173—177. Compare A., 1918, ii, 315).—The replacement of sodium in sodium permutite by silver, and the replacement of silver in silver permutite by potassium, barium, and ammonium have been studied. It is found that shaking permutite with solutions of the various salts for twenty minutes is sufficient to complete the interchange. In all cases except the replacement of silver by barium, the concentration of the solution has no effect on the amount of change. The change between sodium permutite and silver is represented by the equation $([Ag_p]/[Na_p])^{1/64} \times (Na_l/Ag_l) = 1.29$, the indices P and L denoting, respectively, permutite and solution. In the case of silver permutite and ammonium nitrate, the reaction is represented by $(Ag_p/[NH_4]_p)^{1/67} \times ([NH_4]_l/Ag_l) = 37.7$. The replacement of silver by potassium is given by the equation

$$(Ag_p/K_p)^{1/17} \times (K_l/Ag_l) = \text{const.} = 9.9,$$

and the replacement of silver by barium by the formula

$$1.5 = (Ag_p/\sqrt{Ba_p})^{2/3} \times (\sqrt{Ba_l}/Ag_l).$$

The various theories put forward to explain the above-mentioned interchange are discussed in the paper. J. F. S.

Wollastonite (CaO, SiO_2) and Related Solid Solutions in the Ternary System Lime-Magnesia-Silica. J. B. FERGUSON and H. E. MERWIN (*Amer. J. Sci.*, 1919, [iv], **48**, 165—189).—A continuation of work previously published (this vol., ii, 401). In the present paper, the solid phases of the ternary system lime-magnesia-silica are examined. The solid phases were obtained by preparing glasses of the desired composition and crystallising at low temperatures. The solids obtained were heated at various temperatures and the changes noted. The results confirm the earlier work with regard to the wollastonite-diopside solid solutions, namely, that wollastonite will take up a maximum of 17% of diopside to form solid solutions. The existence of solid solutions of pseudowollastonite-diopside containing a maximum of 16% of diopside is confirmed. A new compound, $5CaO, 2MgO, 6SiO_2$, is described. Solid solutions of åkermanite (or perhaps of an unstable compound, $3CaO, MgO, 3SiO_2$) in both wollastonite and pseudowollastonite are shown to exist. The wollastonite solutions extend to a composition containing between 60% and 70% of åkermanite, and the pseudowollastonite solid solutions extend to a composition containing about 23% of the same compound. It is shown that an area exists in which the wollastonite-diopside, wollastonite-åkermanite, and wollastonite- $5CaO, 2MgO, 6SiO_2$ solid solutions are all capable of existence. The decomposition temperatures on this area between the 17% diopside solid solution and the compound $5CaO, 2MgO, 6SiO_2$ pass through a minimum. The compound $5CaO, 2MgO, 6SiO_2$ decomposes at 1365° , and the 17% diopside solid solutions at about 1340° , whilst pure wollastonite undergoes inversion at 1200° .

Further, the inversion temperatures and decomposition temperatures of the solid solutions of silica and the compound $3\text{CaO} \cdot 2\text{SiO}_2$ were studied. The results are discussed generally, and diagrams and models to represent the system are drawn. J. F. S.

Graphic Representation of Systems of the Form $a+b=c$ in Triangular Co-ordinates and a [Method of] Presentation of the Phase Rule. WA. OSTWALD (*Zeitsch. Elektrochem.*, 1919, 25, 251—254).—A mathematical paper in which the representation of systems of the form $a+b=c$ on triangular co-ordinates is considered. The use of such a co-ordination system for the general representation of phase-rule problems is discussed. J. F. S.

Theory of Detonation. R. BECKER (*Zeitsch. Elektrochem.*, 1917, 23, 40—49).—The theory of detonation is developed mathematically, and from the equations deduced the following values are calculated, which are of the same order as the experimentally determined values: for a detonation temperature of 2000° with glyceryl trinitrate, a detonation pressure of 92,500 atms. is set up and the detonation proceeds through the mass with a velocity of 7250 metres per sec.; for 2500° the corresponding figures are 110,500 atm. and 7930 metres per sec. J. F. S.

Development of Atomism. I. M. GIUA (*Gazzetta*, 1919, 49, ii, 1—42).—A historical essay with the headings: Genesis of atomism; precursors of atomism in Greece; doctrine of the elements: Anaxagoras and Empedocles; the atomistic system: Leucippus and Democritus; Plato and Aristotle; atomism of Epicurus; atomistics in the poem of Lucretius; atomistics in the Middle Ages; Arabic atomism. T. H. P.

Harmony of the Atomic Weights. EDUARD SCHMIZ (*Ber. Deut. pharm. Ges.*, 1919, 29, 504—518).—The author calculates numerical relationships between the atomic weights of the elements. These relationships are the same as those which exist between the sides, hypotenuse, and radius of the inscribed circle of an isosceles right-angled triangle, and the radius of the circumscribed circle round the squares erected on the sides of the triangle. The ratios of the named lines are $\sqrt{2}/2:1:(\sqrt{2}-1)/2:\sqrt{5}/2$. Thus in twelve cases it is shown that the ratio of the atomic weights of pairs of elements in the same group of the periodic system is $\sqrt{5}:\sqrt{2}$; in nine other cases the ratio is $\sqrt{5}:\sqrt{5}-1$. In several cases contiguous elements in the same series exhibit the ratio $\sqrt{5}/2:(2\sqrt{2}-1)/2$. Other relationships of a similar character are also given. J. F. S.

Law of Multiple Proportions. E. PUXEDDU (*Gazzetta*, 1919, 49, i, 203—208).—The various forms in which the law of multiple proportions is expressed, including the new statement of this law by Balareff (*A.*, 1918, ii, 15), are discussed. It is shown that the law,

usually illustrated by means of the oxides of nitrogen and by a few other inorganic and organic groups of compounds, possesses an intrinsic significance different from that commonly attributed to it, and that the new mode of enunciating it is a necessary consequence of various principles of general chemistry, and does not correspond exactly with the original enunciation.

T. H. P.

Determination of Molecular and Atomic Weights; the Density of Gases under Normal Conditions and Critical Constants. J. J. VAN LAAR (*J. Chim. Phys.*, 1919, 17, 266—328).

—A critical consideration of the methods of calculating atomic and molecular weights of gases from purely physical data. It is shown that for the majority of gases, on the assumption that $v = \infty$, $a = a_c(e^{a/RT})/(e^{a/RT_c})$ and $b = b_c(e^{a/RT})/(e^{a/RT_c})$, where $a = RT_c$. At 0° $RT_0 = 1$ and $a_0 = (a_c)_\infty e^{RT_c - 1}$ and $b_0 = (b_c)_\infty e^{RT_c - 1}$. On reducing a_c and b_c of the volume v_c to the volume $v = \infty$, the values become $(a_c)_\infty = \phi a_c$ and $(b_c)_\infty = \phi b_c$, where ϕ is given by the expression $\phi = 1 + \epsilon T_c$, in which ϵ has a value 54×10^{-5} for substances with a critical temperature below 300° Abs. and 43×10^{-5} for substances with a critical temperature above 300° Abs. This difference may probably be expressed by an expression of the type $\phi = 1 + \epsilon T_c - \epsilon' T_c^2$. The value $\epsilon = 43 \times 10^{-5}$ may, however, always be used, since the value of B_0 is nearly always relatively very small for substances with a critical temperature below 300° absolute, so that this value has little influence on the value of M . The function $e^{a/RT}$ often appears too large for diatomic gases, and in this case it may be retained if $a = \frac{1}{2}RT_c$ is employed. In the majority of cases where the critical temperature is above 300° $B_0 = b_0 - a_0 = (b_c - a_c) \cdot e^{RT_c - 1} \times (1 + 0.00043T_c)$. In this formula b_c may be calculated from the expression $b_c = RT_c/8p_c$, and a_c from $a_c = RT_c \times b_c \times 27/8 \cdot \lambda$, where the correcting factor λ is obtained from the formula $\lambda = 27/(\delta\gamma - 1)[\gamma/(\gamma + 1)]^2$ and $2\gamma = 1 + 0.038\sqrt{T_c}$. In the case of abnormal substances a_c and b_c may not be calculated by the above simple formulæ, but by means of much more complicated formulæ which are developed in the paper. The formulæ put forward are used to calculate the atomic weights of carbon, xenon, nitrogen, helium, hydrogen, neon, argon, and krypton from physical data, and yield values in excellent agreement with the accepted values.

J. F. S.

Single Deflexion Method of Weighing. PAUL H. M.-P. BRINTON (*J. Amer. Chem. Soc.*, 1919, 41, 1151—1155).—To use this method, the balance is given a permanent overload on the left arm by screwing the adjusting nut on one end of the beam until, when the beam and pans are released, the pointer swings out 3 to 7 divisions to the right. The pan arrests must be so adjusted that there is no lateral vibration of the pans when released, and the method may not be used with balances in which the beam and pans are released by a single operation, such as the turning of a single

milled head or lever. In making a measurement after freeing the beam, the pans are released by a gentle, steady motion, the pointer swings out to the right, and the turning point of the single swing is taken as the zero of the balance. To obtain the weight of any object, it is counterbalanced by weights until on releasing the pans the pointer swings out to the same point. A number of readings made by the author and by students are given to show that exceedingly rapid weighing to within 0.1 mg. is possible by this method.

J. F. S.

Self-acting Mercury Pump. A. Stöck (*Zeitsch. Elektrochem.*, 1917, **23**, 35—40).—A self-acting mercury pump, on the Toepler principle, is described, which permits the collection of the gases pumped off. The movable mercury reservoir is replaced by a strong three-necked bottle into which the foot of the pump enters. The mercury is raised by means of air or carbon dioxide under pressure until the pump is full, then by means of valves actuated by the mercury, the pressure is cut off and the mercury falls again. The pump has the advantage, in addition to the ease of operation, that the mercury does not become contaminated with impurities from rubber connexions between its two main parts.

J. F. S.

Greaseless Valve for Gas Work. A. Stöck (*Zeitsch. Elektrochem.*, 1917, **23**, 33—35).—A modification of the floating valve previously described (A., 1915, ii, 339) is given in the paper. This consists of a pair of narrow tubes ground to fit a constriction in each of two parallel tubes. On raising a mercury reservoir connected with the tubes the valves are raised and close the apparatus. The action is similar to that of the valve in a Toepler pump. Three forms of valve are described which are designed for use in working with gases which have chemical action on the lubricant used with glass taps. These valves are made of a porous material which will allow the passage of gases, but not of mercury, so that when the valve is in contact with mercury no gas may pass. The valves are fitted into the glass parts of apparatus by ground joints. These valves may be used in the production of high vacua, and they exhibit no tendency to absorb gases. They are rather slow in action; thus the pressure in a 1350 c.c. flask filled with air was reduced from 760 mm. to 391 mm. in five minutes, to 189 mm. in fifteen minutes, 73 mm. in thirty minutes, and to 0.0006 mm. in ten hours by means of a mercury pump fitted with a double valve of the type described.

J. F. S.

Gas Washing and Absorption Apparatus. FRITZ FRIEDRICHS (*Zeitsch. angew. Chem.*, 1919, **32**, 252—256).—The author discusses the properties of some thirty different forms of gas-washing and gas-absorption apparatus which have been described since the first Woulfe's bottle was used for the purpose. He considers that only those forms which have a "serpentine" principle ensure complete washing or absorption of a gas under reasonable conditions.

W. P. S.

Simple Distillation and Extraction Apparatus. H. W. VAN URK (*Pharm. Weekblad*, 1919, **56**, 1301—1303).—A description, illustrated by a diagram, of a simple apparatus which may be used alternatively for direct distillation or extraction. W. S. M.

Inorganic Chemistry.

An Electrolytic Hydrogen Generator for the Laboratory.

L. D. WILLIAMS (*J. Soc. Chem. Ind.*, 1919, **38**, 355r).—The cell consists of a filter flask of 250 c.c. capacity fitted with a cork carrying a straight tube 30 cm. long and 1.5 cm. wide. The anode is a strip of lead inside the tube 25 cm. long, the lower end as wide as possible, whilst the remainder is 1 cm. wide. The upper end is soldered to a copper lead which supports the electrode so that its lower end is 1 cm. above the bottom of the tube. The cathode is a strip of lead foil thin enough to pass between the cork and the neck of the flask without causing any leakage. The electrolyte consists of 20% sulphuric acid, and should nearly fill the flask when the exit is open. Such a cell will produce 7 c.c. of hydrogen per ampere per minute. The ideal plant for a small laboratory consists of ten cells run normally at 1 ampere, with a variable resistance, an ammeter, and purifying apparatus. The cell can also be used as a source of oxygen. E. H. R.

Physical Constants of Chlorine under the Action of Light.

A. CAMPETTI (*Nuovo Cim.*, 1919, [vi], **17**, i, 143—158).—Experiment shows that the internal friction and the thermal conductivity of chlorine are not appreciably modified by the light from an arc lamp which has been passed through a dilute solution of copper sulphate to free it from most of the less refrangible radiations. The same is, contrary to the conclusions of Trautz (*A.*, 1912, ii, 746), most probably the case with the thermal capacity, that is, the specific heat at constant volume, of the gas. The value of $\eta \times 10^7$ found for chlorine is 13.28 at 15°. The thermal conductivity of chlorine is about 0.8 times that of air. T. H. P.

The Catalytic Oxidation of Ammonia. PAUL PASCAL and

EUGÈNE DECARRIÈRE (*Bull. Soc. chim.*, 1919, [iv], **25**, 489—507).—Platinum was used as a catalyst in six different states of subdivision, varying from thin platinum foil cut into pieces and made into balls to platinised anhydrous magnesium sulphate. There is a certain minimum temperature for an appreciable velocity of oxidation varying with the physical state of the catalyst. This minimum temperature increases with the curvature of the surface of the catalyst, but is independent of the duration of contact and

of the concentration of the air-ammonia mixture. In every case there is a certain temperature and concentration range over which the maximum oxidation occurs, the yield diminishing outside these limits and becoming insignificant at 900°. In the case where balls of platinum foil were the catalyst, increasing the oxygen content of the air slightly increased the yield. The ammonia not converted into oxides of nitrogen is almost invariably lost as free nitrogen, but there are three exceptions where some of the ammonia passes through unchanged: (1) when the temperature is only about 320°; (2) when the alveolar industrial catalyst is used; (3) when the catalyst is a plug of very fine platinum wire or wool. [See, further, *J. Soc. Chem. Ind.*, 1919, November.] W. G.

Effect of Diminution of Pressure on the Fixation of Nitrogen as Nitric Oxide by means of the Electric Arc. E. BRINER and PH. NAVILLE (*Helv. Chim. Acta*, 1919, 2, 348—352).—As in the formation of ammonia (compare this vol., ii, 148, 190, 338), the optimum yield of nitric oxide from nitrogen-oxygen mixtures under the influence of the electric arc is given when the nitrogen is in excess, when the pressure is low, and when electrodes of certain metals are employed; iron and nickel behave normally, the optimum yield being then obtained with 50% of oxygen, whilst the displacement of the optimum towards the nitrogen-rich mixtures is most marked with platinum and less so with iridium and copper. The actual increases in the yield produced by lowering the pressure and by using excess of nitrogen are less pronounced than in the case of ammonia, but the dependence of the displacement of the optimum yield on a reaction localised in the neighbourhood of the electrodes is more apparent, and is shown only with short arcs and particularly with parallel electrodes. These results are in accord with Guldberg and Waage's law only if the active masses are represented by the concentrations of active particles, and not by the molecular concentrations of the two elements; such active particles are most probably the neutral atoms liberated by the dissociating action of the arc on the molecules. The favourable result obtained by use of excess of nitrogen is explained by the greater resistance to dissociation exhibited by nitrogen molecules. T. H. P.

Alkali Hypochlorites; Free or Combined Salts. Ed. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1919, [vii], 20, 113—115).—Reasons and evidence are adduced to show that alkali hypochlorites have the formula X_2OCl_2 , or $NaOCl \cdot NaCl$, the constituents in the latter formula being combined to form a single molecule. The similarity between the reactions of calcium hypochlorite and alkali hypochlorite favours the combined salt view, as does also the decomposition of calcium hypochlorite by sodium carbonate: $CaOCl_2 + Na_2CO_3 = Na_2OCl_2 + CaCO_3$. The reaction between a hypochlorite and sulphuric acid would be represented by the equation $Na_2OCl_2 + H_2SO_4 = Na_2SO_4 + Cl_2 + H_2O$, whilst the equation

$\text{NaOCl} + \text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{Cl}_2 + \text{H}_2\text{O}$ would be representative of the reaction if the hypochlorite consisted of NaOCl .

W. P. S.

New Compound of Lime and Bromine and a Process for its Manufacture. JOHN STANLEY ARTHUR and LEONARD GIBBS KILLBY (Brit. Pat., 131750).—A new bactericidal compound, $\text{CaO} \cdot \text{CaOBr}_2 \cdot \text{H}_2\text{O}$, having properties similar to bleaching powder, but stable up to 100° , is produced by heating at 100° the red compound, $\text{CaOBr}_2 \cdot \text{H}_2\text{O}$, formed by acting on quicklime with bromine and water in the proportion of 100 grams of the former to 41 c.c. of bromine and 36 c.c. of water. During the heating, bromine and water are evolved, and the new compound remains as a pale yellow powder containing about 33% of available bromine. [See also *J. Soc. Chem. Ind.*, 1919, 843A.] G. F. M.

Some Chemically Reactive Alloys. E. A. ASHCROFT (*Trans. Faraday Soc.*, 1919, 14, 271—277).—Alloys of magnesium and lead containing from 5% to 50% of magnesium and 95% to 50% of lead when exposed to moist air rapidly absorb the whole of the oxygen present. The two metals form the compound Mg_3Pb , and the corresponding alloy, containing 19% of magnesium and 81% of lead, is the most reactive of the series. During the oxidation process, the alloy crumbles to a black powder, a mixture of magnesium hydroxide, $\text{Mg}(\text{OH})_2$, and a hydrate of lead sub-oxide, $\text{Pb}_2(\text{OH})_2$, being formed. These hydrates are stable when heated at 200° . The mixture is unaffected by further exposure to dry air, but in presence of water further oxidation occurs, the lead sub-oxide being oxidised to $\text{Pb}(\text{OH})_2$. With the more reactive alloys, the action takes place in the cold, but with those containing upwards of 35% of magnesium, heat is necessary. The use of these alloys is suggested for removing the last traces of oxygen from gas mixtures, for instance, in the preparation of pure hydrogen for aircraft purposes.

When the alloys are boiled with water, oxidation occurs and free hydrogen is formed. The magnesium is oxidised rapidly, but the formation of lead sub-oxide takes place relatively slowly. When, however, the digestion with water is carried out under pressure at about 150° , the lead is completely oxidised to lead oxide and the theoretical quantity of hydrogen is liberated.

Alloys of magnesium and zinc are far less reactive. In fact, these alloys show greater resistance to oxidation than either magnesium or zinc alone (compare Grube, A., 1905, ii, 320).

E. H. R.

Thorium Lead. O. HÖNIGSCHMID (*Zeitsch. Elektrochem.*, 1917, 23, 161—165).—After a discussion on the atomic weights and origins of the various lead isotopes, the author describes a series of experiments made to determine the atomic weight of the lead extracted from thorite from Ceylon. The method of analysis is the same as that previously described (A., 1914, ii, 653). Four

determinations were made of the ratio $(\text{Th})\text{-PbCl}_2:2\text{Ag}$ and four determinations of the ratio $\text{Th}\text{-(PbCl}_2\text{):}2\text{AgCl}$. From the first set of measurements the value 207.77 is obtained, and from the second set the value 207.78. From both sets the mean value 207.77 ± 0.14 is calculated as the atomic weight of lead from this source. The present value is entirely in agreement with the value determined by Soddy (T., 1914, **105**, 1402) by an indirect method. Assuming the stability of the two isotopes Ra(G) and Th(E) , the author calculates that these two substances are present in the ratio 20:7, or that the lead from thorite consists of 8.9% of uranium-lead and 91.1% of thorium-lead.

J. F. S.

Thallium Selenides. LUIGI ROLLA (*Atti R. Accad. Lincei*, 1919, [v], **28**, i. 355—359).—According to both Pélabon (A., 1907, ii, 688) and Murakami (A., 1916, ii, 34), thallium and selenium form three compounds, the former giving to them the formulae Tl_2Se , TlSe , and Tl_2Se_3 , and the latter Tl_2Se , TlSe , and Tl_2Se_3 . The author's attempts at thermal analysis of this system lead to discordant results, the inapplicability of this method depending on the slowness of the reaction involved or on its inconsiderable heat effect. The more sensitive method, consisting in tracing the variation of the solution tension with change of the composition, has therefore been employed, the results obtained excluding the existence of the third thallium selenide, for which different formulae were given by Pélabon and Murakami.

T. H. P.

Rare Earths. IX. Atomic Weight of Yttrium. III. H. C. KREMERS and B. S. HOPKINS (*J. Amer. Chem. Soc.*, 1919, **41**, 718—721).—The atomic weight of yttrium has been determined by the silver chloride method. The yttrium compound was purified by the sodium nitrite precipitation method (A., 1917, ii, 34), and the product converted into oxalate. The oxalate was ignited in a platinum dish and the oxide dissolved in redistilled nitric acid. The solution was filtered and diluted with 2 litres of "conductivity water" in a Jena flask, and treated with ammonia gas. The precipitated hydroxide was washed by decantation, dissolved in nitric acid, and reprecipitated with oxalic acid. The oxalate was again ignited, and the whole process of purification repeated. The final oxide was moistened with water, and hydrogen chloride passed over until all had dissolved, and, after filtering, the solution was stored in a quartz flask. The method of dehydrating, fusing, and weighing the anhydrous chloride was the same as previously described (*loc. cit.*). The anhydrous yttrium chloride was dissolved in a small quantity of water in a small quartz flask, and the solution transferred to a 5-litre glass bottle, diluted with 2 litres of water, and treated slowly with continuous shaking with the same volume of silver nitrate solution containing the calculated amount of silver nitrate. The bottle and contents were then placed in a shaking machine and shaken for twelve hours. The precipitate was allowed to settle, and the solution tested in a nephelometer for an excess of either chloride or silver ions. Additions of a standard solution

of either silver nitrate or sodium chloride were made until equivalence was obtained, and the solution again shaken for several hours. The whole process was carried out in a dark-room. The precipitation was effected in the above manner because earlier experiments had shown that equilibrium was only slowly attained, and dilute solutions with shaking were important factors in reaching a satisfactory end-point. Experiments were made with seven samples, and from the ratio $3\text{Ag}:\text{YtCl}_3$ the atomic weight of 89.33 was obtained, the extreme values being 89.30 and 89.34.

J. F. S.

Reducing Action of Manganous Oxide. V. MACRI (*Boll. chim. farm.*, 1919, **58**, 201—202).—Manganous sulphate completely precipitates the silver from a hot ammoniacal silver nitrate solution. The white precipitate formed by addition of the manganous salt to ammoniacal mercuric nitrate solution turns grey and then brown on boiling, and, after treatment with sulphur dioxide solution or an acidified solution of a sulphite, leaves a heavy, brownish-grey, pulverulent deposit, which is not dissolved by dilute nitric acid, but is readily attacked by the concentrated acid, with formation of nitrous fumes. When an ammoniacal solution of copper and manganous sulphates is boiled, cuprous oxide is precipitated; the supernatant, colourless liquid gradually becomes blue in the air. Addition of ammonia to a solution containing a cobalt and a manganous salt yields a precipitate of manganous hydroxide which gradually becomes brown, not, however, by direct reduction of the cobalt oxide, since the latter first undergoes peroxidation in the air, and then gives up its oxygen to the manganese, especially on shaking. No tests were made with gold or platinum, but the hydroxides of other metals are not oxidised by manganous salts.

T. H. P.

Corrosion of Metals, especially Rusting of Iron. F. GOUDRIAAN (*Chem. Weekblad*, 1919, **16**, [40], 1270—1285).—The conditions governing the corrosion of metals, especially the rusting of iron, have been investigated by the author. In pure, air-free water the process is purely electrolytic. When the concentration of the Fe^{++} ions in the solution is 1.2×10^{-6} gram-mols. per litre, action ceases. The addition of oxygen produces a very marked effect; the oxidation of the ions gives rise to a fresh *E.M.F.*, and corrosion will continue unless interrupted by a disturbance of the equilibrium of the metal itself. Carbon dioxide is not essential for corrosion; it plays a secondary part only. Nor are the formation and effect of hydrogen peroxide (Traube, A., 1885, 1105) confirmed. In presence of oxygen, the velocity of corrosion $= K(C_0 - C_1)$, C_0 being the solubility of the oxygen in the electrolyte and C_1 its concentration near the iron. Corrosion is greatest where $C_0 = C_1$, that is, where the metal is in contact both with air and water. In weak salt solutions, no effect is observed. Most electrolytes have a maximum "critical" concentration at which corrosion is greatest, but above this concentration the effect diminishes, and many solutions

have also a "limiting" concentration at which corrosion ceases entirely. Tables are given showing values for various electrolytes. Solutions of sodium carbonate above $\pm 0.1N$ strength, and of sodium hydroxide above $0.02N$, are rust-preventive. Ammonium salts generally are very corrosive. The potential of the metal is a dominating factor; an *E.M.F.* of 0.793 volt was obtained with pure iron, which was slightly altered by compression or cooling, but slowly regained its original value. Impurities in iron, by setting up local *E.M.F.*'s up to 20–90 millivolts, accelerate corrosion. The effect of other metals depends on their comparative potentials. Contact with copper increased corrosion of iron by 25–47%, and with nickel by 14–19%. No definite data are obtainable with most metals, however. The composition of rust varies considerably. The author gives many references to the work of other investigators.

W. J. W.

Constitution of Iron-Chromium Alloys. ERNST JÄNECKE (*Zeitsch. Elektrochem.*, 1917, **23**, 49–55).—The system iron-chromium has been examined by means of fusion curves and by the microscopic study of polished sections of the various alloys. The fusion curves were made in a dynamidon (alumina and clay) furnace fitted with a magnesite crucible and heated electrically. The temperatures were automatically recorded by means of a thermo-element and recorder. Curves were produced for six alloys lying between the limits 10Fe:90Cr and 90Fe:10Cr, and all indicate that the system iron-chromium consists of a single eutectic which can form mixed crystals with either component. The eutectic contains 75% of chromium and melts at 1320° ; the limits over which mixed crystals are formed are 55–85% of chromium. The microscopic investigation shows that the crystalline structure is finer the greater the percentage of chromium. The alloys are all tough, and only in the case of the alloys rich in chromium (above 80%) is it possible to break them on an anvil. The alloys are easily scratched by steel and are easily polished. Nitric acid, even when boiling, is without action, but hot 1:1 sulphuric acid attacks them readily. The present results are at variance with previously published results of Treitschke and Tammann (*A.*, 1907, ii, 958), who regard the system as pseudobinary with a single compound of undetermined composition. The author attributes Treitschke and Tammann's results to the presence of aluminium in the chromium used by them.

J. F. S.

Chromium Azoimide. E. OLIVERI-MANDALÀ (*Gazzetta*, 1919, **49**, ii, 43–46. Compare Curtius and Rissom, *A.*, 1899, ii, 90).—Chromium azoimide may be separated by means of the insoluble pyridine compound, $\text{Cr}(\text{N}_3)_3 \cdot 3\text{C}_5\text{H}_5\text{N}$, which forms green, crystalline crusts and explodes violently when heated. When boiled, its concentrated aqueous solution deposits mixtures of basic salts of various compositions, the *basic azoimide*, $\text{OH} \cdot \text{Cr}(\text{N}_3)_2 \cdot 2\text{H}_2\text{O}$, which is far less explosive than the original compound, being isolated. Aqueous solutions containing chromium azoimide exhibit the green colour

peculiar to complex chromium salts, and do not yield a precipitate with ammonia solution; even when the experimental conditions are widely varied, addition of silver nitrate does not cause precipitation of the whole of the nitrogen as silver azoimide.

T. H. P.

The Crystallography of Uranyl Nitrate Hexahydrate. E. QUERCIGH (*Riv. min. crist. Ital.*, 1915, **44**, 6—14).—A detailed description is given of the crystals, which varied widely in habit according to the solvent employed in their formation.

CHEMICAL ABSTRACTS.

New Method of Analysis of Platinum Ores and Compositions of Native Platinites from the Urals. LOUIS DUPARC (*Helv. Chim. Acta*, 1919, **2**, 324—337).—The modes of occurrence and processes of extraction of platinum in the Urals, and a new method for analysing platinum ores, are described; a table is also given showing the mean compositions of samples of platinum from the chief centres in the Urals. [See, further, *J. Soc. Chem. Ind.*, 1919, 822A.]

T. H. P.

Mineralogical Chemistry.

Oceanic Salt Deposits. WILHELM GRÜNEWALD (*Inaug.-Diss. Erlangen*, 1913, 44 pp.; from *Jahrb. Min.*, 1916, ii, Ref. 255).—The work is a continuation of that of van't Hoff and Meyerhoffer, and deals mainly with accurate determinations of the solubility relations of the various salts found in the salt deposits; 1000 mols. H_2O at 25° dissolve 88 mols. KCl , or 111 mols. $NaCl$, or 12 mols. K_2SO_4 ; at 83° , 118 mols. $NaCl$. Magnesium sulphate heptahydrate at 25° , 1000 mols. H_2O contain 55 mols. $MgSO_4$. Potassium chloride and carnallite at 25° , 1000 mols. H_2O contain 72.5 mols. $MgCl_2$ and 11 mols. KCl . Magnesium sulphate heptahydrate and picromerite (sclerite) at 25° , 1000 mols. water contain 58.5 mols. $MgSO_4$ and 5.5 mols. K_2SO_4 . Potassium sulphate and picromerite at 25° , 1000 mols. H_2O contain 22 mols. $MgSO_4$ and 16 mols. K_2SO_4 . Sodium chloride and magnesium chloride hexahydrate at 25° , 1000 mols. H_2O contain 103 mols. $MgCl_2$ and 2.5 mols. $NaCl$.

L. J. S.

An Unlisted Mineral. GEORGE J. HOUGH (*Amer. J. Sci.*, 1919, [iv], **48**, 206).—A new silver-copper mineral, found in a pocket at a depth of 1100 feet in the Cocinera Mine at Ramos, in San Luis Potosi, Mexico, is described. The mineral is silver-grey in colour with a metallic lustre and slowly tarnishes to black; its streak is leaden-grey, and hardness 2.5. It has $D\ 6.14$, and is quite homogeneous. Its composition is: copper, 60.58%; silver, 27.54%; iron, 1.55%; and sulphur, 9.65%, which would give as the empirical

formula AgCu_4S . The author suggests the name *cocimerite* for the mineral. J. F. S.

Exchange of the Bases of Zeolites in Neutral Salt Solutions. ILSE ZOCH (*Chemie der Erde*, 1915, 1, 55 pp., and *Inaug.-Diss.*, Berlin; from *Jahrb. Min.*, 1916, ii, Ref. 266—267).—Various zeolites were shaken in solutions of ammonium chloride. Although the reaction proceeds at first with comparative rapidity, yet equilibrium is only slowly reached. For example, for stilbite in grains of 0.25—0.5 mm. equilibrium is reached after forty to fifty days. Temperature, fineness and quantity of powder, and strength of the solution, all exert an influence. There is an exchange only of the bases, calcium, sodium, and potassium, these being replaced by an equivalent amount of ammonium; alumina and silica do not pass into solution, and the amount of chlorine in the latter remains constant. The substitution is accompanied with a change in the optical characters of the material. Chabazite is most readily acted on, then stilbite, heulandite, and harmotome in the order named, whilst scolecite is scarcely affected. Silver nitrate solution acts readily on stilbite at 50°. Copper chloride solution acts on chabazite, stilbite, and heulandite as shown by a change in the birefringence and the green staining; the latter is removed again when the copper is replaced by ammonium.

L. J. S.

Analytical Chemistry.

New Method of Chemical Analysis. A. W. HULL (*J. Amer. Chem. Soc.*, 1919, 41, 1168—1175).—A method of analysis based on the use of X-rays is described. The method consists in passing a beam of monochromatic X-rays through the powdered material contained in a glass tube and photographing the diffraction pattern produced. The apparatus required consists of a Coolidge X-ray tube fed by a transformer; in front of the tube a screen of suitable metal is placed which acts as a filter (for a molybdenum tube, a zirconium filter is used). The rays passing through the filter are cut down to a narrow beam by means of two lead slits; this beam then passes through the material under analysis, and a fraction of it is scattered. The material is placed at the centre of a photographic film which is bent over a semi-circular strip of wood or brass. After exposure for an hour the film is developed and the photograph compared with photographs prepared from known substances. Substances with a similar crystal structure yield similar patterns, but the intensity and spacing of the individual bands varies with each substance. Examples are given showing that this method is capable of use for analysing mixtures and also gives an approximate quantitative analysis of simple mixtures. J. F. S.

Electrical Apparatus for Use in Electrometric Titrations.

HOWARD S. ROBERTS (*J. Amer. Chem. Soc.*, 1919, **41**, 1358—1362).

—A potentiometer is described for use in electrometric titrations. This instrument does not necessarily give the *E.M.F.* readings in volts, but in arbitrary units, since all that is desired in this type of work is the inflexion point of the *E.M.F.* The instrument consists of a rheostat on which two sliding contacts work. The contacts indicate on scales which are numbered in opposite directions, the one from 0 to 100 and the other from 100 to 200. Thus when the point 100 represents zero potential, readings may be made with a solution which changes the sign of its *E.M.F.* without the use of reversing keys and without introducing a minus sign into the figures. The potentiometer is used with a single dry cell and a high resistance galvanometer.

J. F. S.

Anti-reflux Device Applicable to Evolution Methods of Analysis.

P. L. ROBINSON (*Chem. News*, 1919, **119**, 159—161).

—The apparatus consists of a liquid trap placed between the reaction flask and the absorption vessel; air is admitted through a vertical tube extending into the liquid, when the pressure in the reaction flask diminishes. A similar apparatus for use in the estimation of sulphur in steel is described.

W. P. S.

Colorimetric Scale for the Rapid Estimation of the Free Hydrochloric Acid in Liquids by means of a Solution of Brilliant-green.

MAURICE DELORE and ROCHÉ (*Compt. rend. Soc. Biol.*, 1918, **81**, 646—649).

—Two c.c. of a solution (1:5000) of brilliant-green (tetraethyldiaminotriphenylcarbinyl sulphate) are mixed with 2 c.c. of the liquid under examination, for example, gastric juice, and the free hydrochloric acid is estimated by comparison with a colorimetric scale. The colour changes are, to green (0.005% hydrochloric acid), then to yellowish-green (0.03% hydrochloric acid), and then to a more pronounced yellow tint (0.2% hydrochloric acid). Decolorisation occurs in one to two hours with a 0.1% solution of hydrochloric acid, but no decolorisation occurs with acid at a concentration less than 0.03%. The colorimetric scale is furnished by mixing an unfiltered, aqueous alcoholic solution of methylene-blue (1:100), a filtered, neutral solution of potassium chromate (1:20), an unfiltered, aqueous alcoholic solution of eosin (0.10:100), and water in such proportions as to yield mixtures exhibiting tints corresponding with those produced by 0.025%, 0.05%, 0.075%, 0.10%, 0.15%, and 0.2% solutions of free hydrochloric acid; the mixtures are kept in small, sealed tubes. A solution of brilliant-green in distilled water is used as a control. A solution of brilliant-green becomes more or less turbid when it is mixed with undistilled water. Attempts to reproduce the turbidity in the colorimetric scale by means of soap, tincture of gum benzoin, etc., did not give satisfactory results; there is, however, little difficulty in such cases in comparing the opaque tints with the transparent tints of the colorimetric scale. The comparison of tints should be made rapidly (especially for hydrochloric acid at the

higher concentrations) before decolorisation occurs; comparison is made in diffused light and the tubes of the colorimetric scale should be kept in the dark when not in use. The presence of lactic acid causes little difficulty since the tint which it produces differs (in being nearly turquoise blue) from that due to hydrochloric acid and is much less intense than the latter. The influence of combined hydrochloric acid on the reaction is also practically negligible. This is shown by the concordance between estimations of free hydrochloric acid (in presence of combined hydrochloric acid) by this method and by use of Linossier's reagent and by the fact that a hyperacid gastric juice (after exact neutralisation of free hydrochloric acid) gave only a slight colour change when treated with brilliant-green solution, this change in colour being less intense than that corresponding with the minimum of the scale. This method is especially adapted to use under conditions where the usual laboratory facilities are not available.

CHEMICAL ABSTRACTS.

Estimation of Iodides. PAUL GODFRIN (*Bull. Soc. pharm. Bordeaux*, 1919, 16; from *Ann. Chim. anal.*, 1919, [ii], 1, 295—297).—The method depends on the decomposition of the iodide by potassium dichromate in acid solution, the liberated iodine being titrated with thiosulphate solution. Ten c.c. of a 1% solution of the iodide are treated with 1 c.c. of 10% potassium dichromate solution and 15 drops of hydrochloric acid; 20 c.c. of 10% sodium acetate solution, 50 c.c. of water, and 2 c.c. of starch solution are then added, and the iodine titrated with standardised thiosulphate solution. The method may be applied to the estimation of iodides in urine; the influence of substances which absorb iodine is removed by titrating the sample with iodine before the dichromate is added; the liberation of the iodine in this case is at a maximum in three minutes, and the loss is about 2.5% of the quantity of iodine present. W. P. S.

Estimation of Iodide, Bromide, and Chloride in Presence of Each Other. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 1298—1300).—The total halogen content in a mixture of chloride, bromide, and iodide is determined by precipitation with silver nitrate. Iodide alone is determined by the addition of excess of iodate after acidifying with benzoic acid, and titration of the iodine liberated by means of thiosulphate. Iodide and bromide are estimated as follows: 25 c.c. of *N*/10-solution of potassium iodate, 5 c.c. of *N*-sulphuric acid, and 20 c.c. of water are added to the solution, and the halogen liberated is driven off by boiling in a Kjeldahl flask. Potassium iodide is now added and a few c.c. of sulphuric acid. The iodine liberated is titrated with thiosulphate. The chloride present is then determined by difference. W. S. M.

Detection of the Halogens in Mixtures of their Salts. A. J. JONES (*Chem. and Drug.*, 1919, 91, 52—53).—Traces of iodide in a bromide or chloride may be detected by the nitrite-

chloroform test, using acetic acid in the proportion of 1 c.c. to 1 gram of the salt and 10 c.c. of water. To detect traces of bromide in chloride or iodide, the salt solution is boiled with the addition of a small quantity of potassium permanganate and phosphoric acid, and the vapours brought into contact with fluorescein paper, the appearance of a red coloration on the paper denoting the presence of bromine. Traces of chloride in iodide or bromide may be detected by treating the salt with chloroform and a mixture of permanganate and phosphoric acid until all the iodine or bromine has been liberated and removed by the chloroform. The aqueous solution is then decolorised with sulphurous acid, the chloride precipitated as silver chloride, and the latter identified by its complete solubility in ammoniacal silver nitrate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, November.] W. P. S.

Iodometric Estimation of Sulphurous Acid and Sulphites.

I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 1366—1373).—The accuracy of the iodine method of estimating sulphurous acid has been the subject of much investigation, and there is considerable divergence in the literature on the subject. The author prepared a pure solution of sulphur dioxide, free from sulphate, by washing the gas obtained from copper and sulphuric acid with barium nitrate solution, and dissolving it in air-free water containing 5% of ethyl alcohol, the solution being made *N*/20. When sulphurous acid was added to *N*/10-iodine, and the excess of the latter titrated with sodium thiosulphate, very accurate results were obtained. Titration of the iodine by sulphurous acid from a burette until complete reduction took place was also satisfactory. Addition of sodium carbonate or hydrochloric acid introduced errors of 1.2 to 2.6%, due to oxidation by the air. Inaccurate results are obtained if the iodine is added from a burette to the sulphurous acid, and no improvement is gained by adding mannitol (Ruff and Jeroch, A., 1905, ii, 200), sucrose, or alcohol. Solution of pure sodium sulphite, when added to the iodine, gave accurate results, but errors up to 2.8% arose when the iodine was added to the sulphite solution. Addition of potassium iodide, which acts as a catalyst in oxidation, caused errors up to 3.4%, and with sodium hydrogen carbonate divergencies up to 4% were obtained. The author states that inaccuracies are due to oxidation by the air, and denies the influence or formation of free sulphur in the reaction (Volhard, A., 1888, 192). W. J. W.

Estimation of Sulphates in a Concentrated Electrolyte and the Estimation of Sulphur in Foods. VERNON K. KRIEBLE and AUTREY W. MAGNUM (*J. Amer. Chem. Soc.*, 1919, 41, 1317—1328).—The authors have investigated the sodium peroxide method of estimating sulphur in foods with the double object of preventing firing or explosions during the oxidation and of precipitating completely barium sulphate from the solutions, obtained from the fused material, which have a high concentration

of electrolytes. As the result of a large number of experiments carried out under various conditions, the following method of procedure is recommended: a suitable quantity (2—3 grams) of the material is placed in a nickel crucible of 100 c.c. capacity, mixed with 2—3 c.c. of water, and well stirred with a nickel rod, 5 grams of sodium carbonate are added and well mixed, and then sodium peroxide in small quantities until the whole mass becomes dry and granular. The crucible and contents are carefully heated with a Barthel alcohol lamp until the mixture becomes a brown, homogeneous, fused mass; the mixture is cooled somewhat, and more sodium peroxide added to make a total of 25—26 grams; 3 grams of sodium carbonate are also added and mixed with the peroxide. The crucible is then heated by pointing the flame at a position opposite the level of the contents of the crucible until the first signs of oxidation appear, when the flame is removed and the lid placed in position. After the oxidation is complete, the crucible is heated for a further ten minutes. When the crucible is cool it is placed in 100 c.c. of water and heated until the contents are dissolved, 50 c.c. of concentrated hydrochloric acid are added, and the volume increased to 350 c.c. by the addition of water. The solution is raised to the boiling point and precipitation made with 10 c.c. of 10% barium chloride solution, added by means of a dropper at the rate of 10 c.c. in four minutes. The liquid is kept for forty-eight hours, and then evaporated to dryness, the residue is treated with water, and, after keeping for eighteen hours, the precipitate is collected on a Gooch filter. The results of this method are always high, due to adsorbed material in the precipitate, and should be corrected by an amount which is determined experimentally. The correction is obtained by repeating the estimation with a solution of a known amount of potassium sulphate and finding the amount by which the weight of barium sulphate differs from the theoretical quantity. The difference gives the correction value.

J. F. S.

Acidimetric Estimations in Liquids from Aluminium Sulphate Manufacture. I. BELLUCCI and F. LUCCHESI (*Gazzetta*, 1919, 49, i, 216—241).—The various methods of estimating free and combined sulphuric acid in acid solutions of aluminium sulphate are discussed.

T. H. P.

Alkalimetric Titrations in Presence of Alumina. I. BELLUCCI and F. LUCCHESI (*Annali chim. Appl.*, 1919, 11, 199—204).—The literature of the subject is discussed and criticised (see preceding abstract).

T. H. P.

The Micro-estimation of Nitrogen by Direct Nesslerisation, and of Total Solids, in Drop Quantities of Human Blood. AMOS W. PETERS (*J. Biol. Chem.* 1919, 39, 285—298).—The estimation of total solids is made by evaporating the known weight of blood, previously diluted with 0.5% sodium fluoride solution, on a weighed quantity of pure talc powder at 75°.

The method of carrying out the digestion of the blood in the micro-Kjeldahl process is minutely described, the most important point in the management of the digestion relating to the process of heating. The colour comparison in the subsequent nesslerisation is made against a single fixed colour standard prepared from picric acid and ferric ammonium sulphate. The conditions of accuracy have been tested, and the method is regarded as trustworthy.

J. C. D.

Estimation of Ammonia in Blood. OTTO FOLIN (*J. Biol. Chem.*, 1919, **39**, 259—260).—It is pointed out that the method employed by Morgulis and Jahr (this vol., ii, 371) yields unsatisfactory results unless every reagent used, including the permutoite, is absolutely free from ammonia. A method is given for rendering preparations of metaphosphoric acid free from ammonia. When the purified reagents are employed, the amount of ammonia obtained from protein-free blood filtrates is practically nothing, only a greenish-yellow colour being obtained with Nessler's reagent.

J. C. D.

Volumetric Estimation of Hydroxylamine. WILLIAM C. BRAY, MIRIAM E. SIMPSON, and ANNA A. MACKENZIE (*J. Amer. Chem. Soc.*, 1919, **41**, 1363—1378).—The authors have investigated three methods for the volumetric estimation of hydroxylamine: (1) the reduction of hydroxylamine to an ammonium salt by an excess of a titanous salt in acid solution, (2) the oxidation of hydroxylamine to nitrous oxide by an excess of ferric sulphate in sulphuric acid solution with titration of the ferrous salt produced, by potassium permanganate solution, and (3) the oxidation of hydroxylamine to nitrous oxide by iodine in a solution kept neutral by means of disodium hydrogen phosphate. The first two methods are found to be accurate, but the iodine method is unsatisfactory. In addition to the known positive error in the ferric salt method, which is due to the addition of permanganate while some hydroxylamine or an intermediate product, nitroxyl, is still present, a negative error due to oxygen of the air is found under certain conditions. Both errors are easily avoided, the latter by adding the hydroxylamine slowly to a boiling solution of ferric sulphate. Three sources of error are met with in the iodine method: (1) that due to incomplete reaction, which may be avoided by the addition of disodium hydrogen phosphate, (2) nitrite formation, which occurs under all the conditions investigated and constitutes a positive error, and (3) absorption of oxygen from the air, which constitutes a negative error. An empirical method is described whereby theoretical results can be obtained by the iodine method, but this is shown to be due to a compensation of the last-named two errors. Hydroxylamine is oxidised mainly to nitrate by an excess of hypochlorous acid. Sodium thiosulphate in a solution of disodium hydrogen phosphate can be quantitatively oxidised to sulphate by iodine. The reaction is rapid at 70°.

J. F. S.

Influence of Fluorides on the Oxidimetric Estimation of Nitrous Acid. I. BELLUCCI (*Gazzetta*, 1919, **49**, i, 209—216).

—Lunge's method of estimating nitrous acid by means of permanganate leads to fallacious results if the solution contains also fluorine ions in high concentration. This anomaly is due to the same cause as that observed by Müller and Koppe (*A.*, 1910, ii, 957) in the oxidimetric estimation, also in presence of fluorides, of manganese by Volhard's method, namely, the formation of derivatives of tervalent manganese. In the case of nitrous acid, this inconvenience may be overcome by treating the nitrous acid, in a solution acidified with sulphuric acid, with excess of standard permanganate solution, then adding, after a couple of minutes, potassium iodide solution and estimating the iodine liberated by the excess of permanganate by titration with thiosulphate solution. A blank estimation should also be carried out with the same volume of permanganate as is used to oxidise the nitrous acid.

The case studied by Müller and Koppe is not amenable to this procedure, since addition of the alkaline iodide would there result in liberation of iodine in amount corresponding with the quantity of permanganate initially taken.

T. H. P.

Estimation of Citrate-soluble Phosphoric Acid by Petermann's Method. H. NEUBAUER and E. WOLFERTS (*Landw. Versuchs-Stat.*, 1916, **89**, 197—202).—New methods are described for preparing Petermann's ammoniacal citrate solution and for applying it to the estimation of the citrate-soluble phosphoric acid of dicalcium phosphate ("Methodes suivies dans l'analyse des matières fertilisantes," Gembloux, 1897). [*See J. Soc. Chem. Ind.*, 1919, 837A.]

T. H. P.

Electrolytic Resistance Method of Estimating Carbon in Steel. J. R. CAIN and L. G. MAXWELL (*J. Ind. Eng. Chem.*, 1919, **11**, 852—860).—A rapid method of estimating carbon in steel has been based on the absorption of the carbon dioxide, obtained by direct combustion, in barium hydroxide solution, and measuring the change in the electrolytic resistance of the solution caused by the precipitation of the barium ions. A simple form of absorption apparatus has been devised for this purpose, containing a cell in which the electrodes can be adjusted so as to give a definite cell constant, and Weibel's galvanometer has been found an accurate instrument for measuring the resistance. The combustion is carried out in an electric furnace, and the carbon dioxide is expelled by a current of air (freed from carbon dioxide). A table showing the percentages of carbon corresponding with the resistance and the temperature of barium hydroxide solutions of definite concentrations has been made, and from this a nomographic chart has been constructed whereby the percentages may be read directly with an error of less than 0.005% of carbon. [*See further, J. Soc. Chem. Ind.*, 1919, 773A.]

C. A. M.

Detection of Carbon Monoxide in Air. DESGREZ and LABAT (*Acad. med.*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 294—295).—Strips of filter paper are immersed in 10% palladium

chloride solution and then dried in the dark. If a strip, moistened at one end, is suspended in air containing carbon monoxide, the moistened portion becomes grey, brown, or black within six minutes, whilst the dry portion retains its yellow colour. The depth of the coloration depends on the amount of carbon monoxide present; 1 part in 1300 parts of air yields a distinct grey coloration. If the air also contains hydrogen sulphide, the strip should be suspended in a bottle through which the air, previously passed over lead acetate, is aspirated.

W. P. S.

Estimation of the Reaction of Natural Waters. J. TILLMANS (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 1—16).—The reaction (hydrogen ion concentration) of most natural waters is due to free carbon dioxide and to carbon dioxide combined as hydrogen carbonates, and is conveniently expressed as ten thousandths of a mg. per litre ($=h'$). In neutral waters $h'=1$; all values above 1 indicate an acid reaction and all values under 1 an alkaline reaction. Generally, h' can be calculated with sufficient accuracy by multiplying the mg. of free carbon dioxide per litre by 3 and dividing the result by the number of mg. of carbon dioxide present as hydrogen carbonate per litre of water. The exceptions to this rule are described. In the case of alkaline waters, the alkalinity may be expressed as the reciprocal of h' . [See, further, *J. Soc. Chem. Ind.*, 1919, November.]

W. P. S.

Acidosis. XVI. Estimations of Bicarbonate in the Blood Plasma of Different Species by the Titration and Carbon Dioxide Capacity Methods. EDGAR STILLMAN (*J. Biol. Chem.*, 1919, **39**, 261—265).—The methods employed were those described by van Slyke, Stillman, and Cullen (*A.*, 1917, i, 521; this vol., ii, 298), and examinations of plasma from the blood of man, dogs, sheep, rabbits, and chickens were carried out. Results obtained by titration agreed with those by the carbon dioxide capacity method, as a rule, within less than two millimolecular in plasma bicarbonate concentration. The results confirm the conclusion reached in the former paper that the two methods may be used interchangeably for clinical and for many experimental purposes.

J. C. D.

The Estimation of Calcium and Magnesium in Different Saline Solutions. E. CANALS (*Bull. Soc. Chim.*, 1919, [iv], **25**, 90—94).—Experiments in which magnesium ammonium phosphate was precipitated by adding a solution of magnesium sulphate to an ammoniacal solution of sodium phosphate containing ammonium chloride showed that considerable excess of phosphate, ammonia, or ammonium chloride or of all three together may be used without the accuracy of the magnesium estimation being thereby affected. Only in special circumstances can magnesium be estimated as oxide or sulphate. Both these compounds are very hygroscopic, and magnesium sulphate is subject to decomposition at a bright red heat.

E. H. R.

Separation and Estimation of Magnesium in the Presence of Fixed Alkalis. P. NICOLARDOT and F. DANDURAND (*Rev. Met.*, 1919, 16, 193—199).—The most trustworthy method for the separation of magnesium from alkalis consists of precipitating the magnesium by means of ammonium phosphate; the details of this method are too well known to need description. A large excess of ammonium phosphate should be avoided; the small excess which is necessary may be removed subsequently by treatment with ferric chloride and ammonia, and the alkalis may then be estimated. Separation of the magnesium by means of ammonium carbonate in alcoholic solution, barium hydroxide, calcium hydroxide, ammonium oxalate, or mercuric oxide is untrustworthy. A simple method for the estimation of magnesium when alkalis are not present (for example, in the analysis of metallic magnesium and its alloys) depends on the precipitation of the magnesium as magnesium fluoride-hydrofluoride; the magnesium chloride, in neutral solution, is treated with a slight excess of ammonium fluoride, the mixture is evaporated to a syrup on a water-bath, and the residue ignited. The ignited residue consists of magnesium fluoride. This method cannot be employed when alkali chlorides are present in the solution. W. P. S.

Estimation of Metallic Zinc Content of Zinc Dust. W. F. EDWARDS (*Chem. and Met. Eng.*, 1919, 21, 192).—Neither the hydrogen-gas method nor the reduction of potassium iodate is on the whole suited to the evaluation of zinc dust, used or unused, in sherardising. The amalgam method is not satisfactory for practical purposes, even if carried out with careful attention to details in parallel estimations under identical conditions. The reduction of ferric sulphate gives inconsistent results, but with crystallised ferric ammonium sulphate satisfactory results are obtained, the time required being approximately fifteen minutes against six to thirty-six hours for the gas method. The method is as follows: 1 gram of zinc dust is put into a 600 c.c. Erlenmeyer flask, together with 50 grams of ferric alum in crystals and 100 c.c. of water, the whole being constantly stirred. As soon as the zinc dust is dissolved, 100 c.c. of 1:10 sulphuric acid are added, and the solution titrated against potassium permanganate. Comparisons of results obtained on new and used zinc dust by the hydrogen-gas method and the ferric alum method are given, and show good agreement. T. H. B.

Simple Method of Analysing Bearing Metal and Similar Alloys. G. OESTERHELD and P. HONEGGER (*Helv. Chim. Acta*, 1919, 2, 398—416).—The principles on which the method described is based are as follows. The alloy is dissolved in boiling concentrated sulphuric acid, dissolution being complete in a few minutes even with an alloy rich in lead. The antimony passes quantitatively into solution in the tervalent form and the tin as stannic sulphate. The copper and lead are converted entirely into copper and lead sulphates, subsequent dilution with water resulting in the separa-

tion of crystalline lead sulphate, which is readily removed by filtration through a Gooch crucible. In the filtrate the antimony is titrated directly with potassium bromate, the titrated solution being then reduced and the tin, and afterwards the copper, estimated volumetrically. In presence of tin, antimony, and lead, copper may be estimated in a few minutes by a simplified form of electrometric titration with sodium thiosulphate. [See *J. Soc. Chem. Ind.*, 1919, 824A.] T. H. P.

Estimation of Small Quantities of Mercury in Toxicological Investigations. F. CARRESCIA (*Boll. chim. farm.* 1919, 58, 242—244).—Descriptions are given of the methods applied to the estimation of mercury in two cases of attempted poisoning by addition of mercuric chloride to coffee and to a bronchial remedy. [See *J. Soc. Chem. Ind.*, 1919, November.] T. H. P.

A Sensitive Reaction for Manganous Salts. D. H. WESTER (*Pharm. Weekblad*, 1919, 56, 1289—1290).—The author points out that the potassium oxalate test for manganese salts is less sensitive than the tests with lead peroxide and nitric acid, and with persulphate and silver nitrate, both of which are applicable in presence of considerable quantities of chlorides. The reaction may, however, be used as a sensitive test for oxalate. W. S. M.

Estimation of Manganese in Steel by means of Persulphate in the Presence of Chromium and Tungsten. P. NICOLARDOT and A. LEVI (*Rev. Met.*, 1919, 16, 201—216).—Investigation of the persulphate method showed that the most trustworthy results are obtained under the following conditions. A quantity of 0.2 gram of the steel is dissolved in 10 c.c. of 33% sulphuric acid and 0.5 c.c. of nitric acid; the solution is then cooled, 5 c.c. of saturated silver sulphate solution and 0.5 gram of persulphate are added, the solution is diluted to 50 c.c., heated for three to five minutes in a water-bath, the heating being discontinued when the red coloration appears. The mixture is set aside until cold and then titrated with arsenious acid solution; the latter should contain 0.5 gram of arsenious acid and 2.5 grams of sodium hydrogen carbonate per litre, and be standardised against a steel containing a known amount of manganese. If the titrated mixture is again heated, the manganese is reoxidised (a sufficient quantity of persulphate still remains for this purpose), and the titration may be repeated. If the steel contains a large quantity of chromium and less than 1% of manganese, the amount of the latter should be brought up to about 1% by the addition of manganese, in the form of a standard permanganate solution, after the treatment with persulphate. The following method is recommended in the case of a steel containing chromium, tungsten, and vanadium. A weighed amount of 0.2 gram of the steel is boiled with 25% sulphuric acid and 0.5 c.c. of nitric acid until a precipitate of yellow tungstic acid forms and all black particles disappear; the mixture is cooled, sodium hydroxide is added in quantity sufficient

to dissolve the tungstic acid and, precipitate the iron, 3 c.c. of phosphoric acid solution (containing 38% P_2O_5) are added, the mixture again cooled, and slightly acidified with sulphuric acid. If the solution thus obtained is not perfectly clear, the estimation must be recommenced. The solution is then treated with 10 c.c. of saturated silver sulphate solution and 1 to 3 grams of persulphate, heated on a water-bath for three to five minutes, cooled, 0.002 gram of manganese (in the form of potassium permanganate solution) is added, and the solution is titrated with arsenious acid solution. The quantity of manganese added is deducted from the result obtained. The authors do not think it advisable to attempt to estimate the chromium and the manganese in the same portion of the sample.

W. P. S.

Estimation of Iron in Iron Ores by means of Permanganate. R. SCHWARZ (*Chem. Zeit.*, 1919, **43**, 499—500).—A reply to Brandt (this vol., ii, 373).—The author maintains that the use of sodium silicate in the titration is trustworthy under the conditions described by himself and Rolfes (this vol., ii, 170).

W. P. S.

Electrometric Titrations, with Special Reference to the Estimation of Ferrous and Ferric Iron. J. C. HOSTETTER and H. S. ROBERTS (*J. Amer. Chem. Soc.*, 1919, **41**, 1337—1357).—Experiments are described on the estimation of ferrous iron by titration with potassium dichromate and potassium permanganate in which the end-point of the reaction is obtained from the *E.M.F.* of the solution against a calomel electrode. The work is extended to the estimation of ferric iron by means of stannous chloride and the titration of potassium dichromate with stannous chloride. The electrical apparatus used in the work is that described by Roberts (see this vol., ii, 471). A special "titration head" is used to cover the flasks in which the titration is carried out. This consists of a glass cap with three openings at the top; through the first opening a glass tube from the calomel electrode enters, the second opening admits the tip of the burette, and the third carries a platinised platinum electrode and admits a current of carbon dioxide. Using this method, solutions of potassium dichromate as dilute as 0.0005*N* may be employed. The electrometric method makes it unnecessary to remove the excess of a reducing agent which has been added in the reduction of a ferric salt. Conditions, such as acidity, need not be controlled except within very wide limits, and hydrochloric, sulphuric, or hydrofluoric acid may be used. The sensitiveness and accuracy of the method make possible the estimation of a few tenths of a milligram of tin, chromium, ferrous, or ferric iron in the presence of large quantities of some other elements, and its use in the blank estimations involved in some of the ordinary estimations by reducing or oxidising agents. The time within which an estimation can be carried out is greatly shortened. The content of ferrous and ferric iron in a silicate, for example, can be deter-

mined in from fifteen to thirty minutes. The precision attainable is comparable to the best of the ordinary volumetric methods.

J. F. S.

New Method for the Estimation of Chromium. A. TERNI and P. MALAGUTI (*Gazzetta*, 1919, **49**, i, 251—256).—The method previously given for the detection of chromium (A., 1913, ii, 881) is applicable to the estimation of this metal, the procedure being as follows. The solution of the chromic salt is boiled with 20 c.c. of nitric acid (D 1.4) and about 1 gram of lead dioxide in a covered 200 c.c. beaker until the volume is reduced to a few c.c. The liquid is then diluted with 40—50 c.c. of water, treated with sufficient 25—30% sodium hydroxide solution to redissolve the precipitated lead chromate, heated to incipient boiling, and filtered into a conical litre flask, the residue on the filter being washed five or six times with boiling water rendered slightly alkaline with sodium hydroxide. The filtrate is diluted to 150—200 c.c., sufficient nitric acid (D 1.2) absolutely free from nitrous acid being added to dissolve the lead chromate almost completely, and then a further 25 c.c. of the same acid. The acid liquid is treated with 5—10 c.c. of 10% potassium iodide solution, and the iodide liberated titrated with sodium thiosulphate solution containing about 25 grams per litre, previously standardised, in presence of 25 c.c. of the nitric acid of D 1.2, by means of $N/10$ -potassium dichromate solution. The method gives good results and is not invalidated by the presence of iron, manganese, or aluminium.

T. H. P.

Rapid Method of Estimating Uranium in Carnotite. C. E. SCHOLL (*J. Ind. Eng. Chem.*, 1919, **11**, 842).—The difficulties of separating uranium in the presence of iron, aluminium, and vanadium, which are the principal impurities in carnotite, are obviated by adding an excess of ferric iron to the solution, precipitating the iron, vanadium, and most of the aluminium with sodium carbonate at about 90°, and then precipitating the uranium from the boiling filtrate by means of sodium hydroxide. The precipitate is dissolved in dilute nitric acid, the uranium again precipitated by means of ammonia at 90°, and the precipitate ignited and weighed as uranium oxide, U_3O_8 . [See, further, *J. Soc. Chem. Ind.*, 1919, 778A.]

C. A. M.

Rapid Method for the Estimation of Titanium in Titaniferous Iron Ores. JOHN WADDELL (*Analyst*, 1919, **44**, 307—309).—The ore is fused with sodium peroxide in an iron crucible, the mass dissolved in water and sulphuric acid, tartaric acid is added, and the iron precipitated as sulphide by means of hydrogen sulphide and ammonia. After removal of the iron sulphide, the solution is boiled with the addition of sulphuric acid to expel hydrogen sulphide, and the titanium then precipitated by means of "cupferron" (the ammonium salt of nitrosophenylhydrazylamine), or the titanium may be estimated colorimetrically by

hydrogen peroxide. [See, further, *J. Soc. Chem. Ind.*, 1919, 775A.] W. P. S.

Estimation of Zirconium as Phosphate. P. NICOLARDOT and A. RÉGLADE (*Ann. Chim. anal.*, 1919, [ii], 1, 278—281. Compare this vol., ii, 180).—Zirconium may be precipitated quantitatively from a 10% sulphuric acid solution by means of ammonium phosphate; two hours should elapse before the precipitate is collected. Aluminium, iron, chromium, and nickel do not interfere, but the iron should be reduced to the ferrous condition before the zirconium is precipitated. Titanium must not be present. Bismuth is precipitated as phosphate from an acid solution, but this metal rarely occurs with zirconium. W. P. S.

Modified Method for the Analysis of Mixtures of Ethylene and Acetylene. WILLIAM H. ROSS and HARLAN L. TRUMBULL (*J. Amer. Chem. Soc.*, 1919, 41, 1180—1189).—A method of estimating acetylene in mixtures with ethylene and other singly or doubly linked hydrocarbons, based on observations of Chavastelon (*A.*, 1897, i, 545), is described. When acetylene is passed into an excess of a neutral solution of silver nitrate, the solution becomes acid, on account of the reaction $C_2H_2 + 3AgNO_3 = C_2Ag_2.AgNO_3 + 2HNO_3$. The method described consists in shaking a measured volume of the gaseous mixture with a 5% solution of silver nitrate and determining the acidity by titration with standard sodium hydroxide. The titration is effected as follows: after absorption is completed, sodium hydroxide is added to the solution containing the precipitated silver acetylide until the brown colour of silver oxide appears; the excess of silver is then precipitated with 20% sodium chloride solution, and the excess of free alkali in solution finally estimated by titration with standard hydrochloric acid, using methyl-orange as indicator. The method is rapid, accurate, and simple of manipulation, and has the added advantage of giving accurate results for acetylene in mixtures of ethylene or of a gas of such similar properties as vinyl bromide, which is readily absorbed by bromine, fuming sulphuric acid, and by neutral or ammoniacal silver nitrate. J. F. S.

Analysis of Sulphonyl Chlorides of Aromatic Substances. F. NEITZEL (*Chem. Zeit.*, 1919, 43, 500).—Three grams of the powdered substance are mixed with 10 c.c. of water, and free sulphonic acids and mineral acids are neutralised with sodium hydroxide solution, using phenolphthalein as indicator; an excess of *N*/1-sodium hydroxide solution and 20 c.c. of alcohol are then added, the mixture is heated under a reflux apparatus for fifteen minutes, and the excess of alkali is titrated. The quantity of alkali used for the hydrolysis is a measure of the amount of sulphonyl chloride present. W. P. S.

Detection of Methyl Alcohol. HANS WOLFF (*Chem. Zeit.*, 1919, 43, 555).—The presence of higher alcohols in ethyl alcohol

renders the detection of methyl alcohol in the latter untrustworthy if the method used depends on the oxidation of the methyl alcohol and identification of the resulting formaldehyde; the higher alcohols, on oxidation, yield substances which give the same coloration with the morphine-sulphuric acid reagent as does formaldehyde (compare Salkowski, this vol., ii, 249). If, however, apomorphine is used in place of morphine in the test, formaldehyde yields a bluish-violet coloration, whilst the oxidation products of the higher alcohols give a yellow or reddish-brown coloration.

W. P. S.

Estimation of Cyanides, Cyanates, and Bromides Present Together. GIUSEPPE VELARDI (*Boll. chim. farm.*, 1919, 58, 241).—Titration with silver nitrate solution gives, in alkaline solution, the cyanide; in solution neutralised with acetic acid, the bromide, cyanide, and cyanate together; in solution acidified with nitric acid, the cyanide and bromide. [See *J. Soc. Chem. Ind.*, 1919, 815A.]

T. H. P.

A Method of Tissue Analysis: Applied to the Posterior and Anterior Lobes of Cattle Pituitaries. C. G. MACARTHUR (*J. Amer. Chem. Soc.*, 1919, 41, 1225—1240).—A modification of Koch's method of tissue analysis is described in which the amount of material required is usually only 10 grams, but may be as low as 2 grams (compare A., 1910, ii, 78—79). The constituents are separated into three groups, proteins, lipins, and extractives, and many instructive determinations made on aliquot parts of each fraction.

The material is first left for several weeks with alcohol, then heated to the boiling point on a few occasions during several days, and finally filtered through a weighed, paper-lined, perforated crucible into a tared beaker, the residue being rinsed with hot alcohol a few times. The residue is next left overnight with ether, warmed several times, and again filtered, using the same crucible and beaker. It is then finely ground and digested with small volumes of hot water, the extract being filtered through the same crucible into a different beaker, evaporated to about 5 c.c., diluted with alcohol, boiled to coagulate the protein, and filtered into the first beaker. All the residues are then transferred by means of alcohol to the crucible, which is placed in a continuous extractor and digested with 95% alcohol for thirty hours, and with chloroform for ten hours. The residual protein is heated in an oven at 105° to constant weight, and the various extracts evaporated in the tared beaker to give the weight of extractives plus lipins. The dried extract is then made into an emulsion with about 40 c.c. of water, treated with 0.5 c.c. of hydrochloric acid to precipitate lipins, centrifuged, and the clear liquid decanted into a 100 c.c. flask containing 5 c.c. of chloroform, shaken, and the aqueous portion poured off into another centrifuge tube, centrifuged, and the clear solution transferred to a second 100 c.c. flask. The lipin residue is treated in the same way with two smaller portions of dilute hydrochloric acid, and finally dissolved in a mixture of alcohol and

chloroform (10:1) in the first 100 c.c. flask, and the volume made up to the mark. The aqueous solution is also made up to 100 c.c.

The further examination of the three fractions follows the usual methods of biochemical analysis, of which the following is a summary. *Extractives*.—(1) Dry weight, ash, and with this any desired inorganic constituents, such as calcium and magnesium. (2) Total nitrogen, by the Kjeldahl method. (3) Nitrogen as ammonia, by rendering a portion slightly alkaline and aspirating the ammonia into 0.01N-acid, after which urease is added to the neutralised liquid and nitrogen as urea estimated. (4) Amino-nitrogen, by Van Slyke's micro-method. (5) Creatine and creatinine, by the picric acid, colorimetric method. (6) Uric acid, by the Folin and Denis colorimetric method (A., 1913, ii, 162, 444). (7) Sugar and other substances which reduce Fehling's solution. (8) Total sulphur and sulphur as sulphates. (9) Total phosphorus and phosphorus as phosphates. *Lipins*.—A portion of the solution is evaporated to dryness, hydrolysed by boiling with dilute hydrochloric acid, and thus differentiated into a lipin residue, which is redissolved in chloroform, and a hydrolysis filtrate. Total nitrogen, sulphur, and phosphorus are estimated in the residue, and the filtrate is examined as follows. (1) Total nitrogen. (2) Amino-nitrogen. (3) Volatile amine nitrogen, and, with the same portion, choline nitrogen. (4) Iodine absorbed, by Hübl's method. (5) Total sulphur. (6) Sugar, by the picric acid method. The original lipin solution is also used for the estimation of phosphorus, nitrogen, sulphur, calcium, the iodine value, and also cholesterol, by Bloor's method (A., 1917, ii, 275). *Proteins*.—Phosphorus, sulphur, calcium, chlorine, and total nitrogen are estimated as usual and then the further differentiation is made by Van Slyke's improved method (A., 1915, ii, 851), the nitrogen being recorded as (1) humin nitrogen, (2) ammonia nitrogen, (3) basic nitrogen, (4) arginine nitrogen, (5) histidine nitrogen, (6) lysine nitrogen, (7) cystine nitrogen, (8) mono-amino-nitrogen, (9) non-amino-nitrogen, and (10) α -amino-nitrogen.

The example of the application of this method which is described, is the analysis of the pituitary lobes. The anterior lobe contains 2.4% more solid matter and 4% more protein than the posterior lobe, but there is a great similarity between the proteins of the two lobes. The posterior lobe is 0.9% richer in lipins, these resembling the lipins of the grey matter of the cortex, and also contains 0.9% more extractives, the excess being largely due to non-phosphate phosphorus, amino-nitrogen, and undetermined nitrogen. Both lobes resemble each other so closely that, in spite of their different origin, it may be assumed that they develop together.

J. C. W.

mations based on the hypothesis that all excess of hydroxide was contained in the lye and not in the curd proper. As may be shown theoretically, this leads to a perfectly defined result for the value of the hydration. This we term the pure "curd" calculation.

The results for sodium palmitate salted out by sodium hydroxide are given in table IV. The pressure was different in each case, since it depended on the condition of the filter bed, pressure being applied until the curd began to be forced through. (In one or two cases some carbon was mixed with the curd.) Several samples at different levels were taken for analysis in some of the experiments. Table V gives similar data for the pressed curds of Experiments 15 and 16 of table II.

TABLE V.

No. of expt.	Curd composition: 100 grams contain			Method of calculation.	Hydration: mols. H ₂ O to 1 NaP.
	NaP.	NaOH.	NaCl.		
15	80.01	0.144	0.761	"Mixed"	2.2
16	80.43	0.160	0.922	"Mixed"	2.2

On examining the results of tables IV and V it appears that the very great pressure to which the curds were subjected while in contact with residual lye lowers the degree of hydration to about half of that of the unpressed curd. This is in accordance with the recognised property of colloids that the swelling pressure increases enormously as the solvent is removed, although the pressures here employed far transcend those hitherto investigated.

The most effective way of dehydrating soap curd is to press it on a porous tile, thus making use of the swelling pressure of kaolin to abstract the water. Curds from Experiments 2 and 6 so treated and the composition calculated as before, gave values for apparent hydration of 1.3 and -1.8 mols. of water respectively; this appears to show that the residual lye had also been greatly concentrated in the process owing to hydroxide being left when the water was absorbed.

Summary.

Marked negative sorption of sodium hydroxide occurs when soap is salted out by sodium hydroxide in concentrated solution.

From the extent of this effect the amount of water contained in the solid part of the curd, as distinguished from the entangled lye clinging to it, may be deduced. Soap curd is thus shown to be a mechanical mixture of hydrate (or sorption compound) and unmeshed lye.

The degree of hydration varies with the concentration of lye as follows:

Lye.	Sorption compound.	Percentage of fatty acid.
3.0N	NaP,3.2H ₂ O	76.28
2.5	NaP,4.4H ₂ O	71.67
1.9	NaP,5.2H ₂ O	68.89
1.5	NaP,6.5H ₂ O	64.81

Extreme pressure lowers the degree of hydration considerably.

In conclusion, we have pleasure in thanking the Colston Society of the University of Bristol for a generous grant towards the purchase of materials and apparatus.

THE CHEMICAL DEPARTMENT,
BRISTOL UNIVERSITY.

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CXXI.—*Reaction of the Potassium Salts of 2-Thiol 5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole and 2 : 5-Dithiol-1 : 3 : 4-thiodiazole with Halogenated Organic Compounds.*

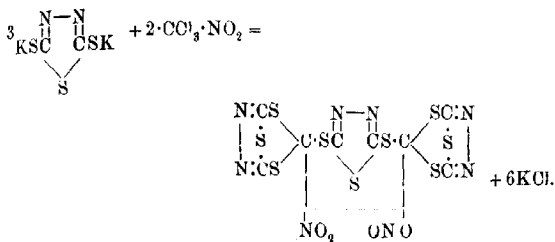
By PRAFULLA CHANDRA RÂY, PRAFULLA CHANDRA GUHA, and
RADHA KISHEN DAS.

GABRIEL (*Ber.*, 1877, **10**, 185) and Holmberg (*Ber.*, 1907, **40**, 1740) treated sodium ethylmercaptide with chloroform and obtained ethyl orthotrithioformate, CH(SET)₃. In the present investigation, it will be shown that the potassium atom of the complex cyclic mercaptides named in the title is singularly reactive towards the halogen atoms of organic compounds of divers types. Thus, chloroform, bromoform, and iodoform yield compounds with the potassium monomercaptide, which may be represented by the general equation $3RK + CHX_3 = 3KX + CHR_3$, where X represents a halogen atom and R the radicle of the complex mercaptide. Chloropicrin acts exactly like chloroform, but is far more reactive than the latter, and the reaction may be expressed by the equation $3RK + NO_2 \cdot CCl_3 = NO_2 \cdot CR_3 + 3KCl$.

The behaviour of tribromoresorcinol, benzylidene chloride, mono-chloroacetic acid, and ethylene bromide has also been found to be of an identical nature. The potassium salt of 2:5-dithiol-1:3:4-

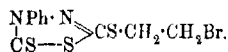
thiodiazole, on the other hand, acts almost as an inert substance towards chloro-, bromo-, and iodo-form.

It is evident that the presence of the two $\cdot\text{SK}$ groups of the dimercaptide exercises a sort of inhibitory influence on the halogen atoms. The reactivity of these halogenated compounds can, however, be materially enhanced by substituting the remaining hydrogen atom by a nitro-group. For instance, chloropicrin acts very readily on the dimercaptide even in the cold. The introduction of an additional negative group has thus a marked effect. The reaction may be represented as follows:



Nitrous fumes escape during the reaction, and an atom of oxygen, as shown above, forms the connecting link between the two carbon atoms of the residues of two molecules of chloropicrin.

Ethylene bromide acts on the potassium monomercaptide; only one atom of bromide combines with the potassium atom, resulting in the formation of the compound,



Monochloroacetic acid, benzylidene chloride, and ethylene bromide no doubt act on the dimercaptide, but the products of the reaction are insoluble in the ordinary solvents, and thus cannot be purified.

EXPERIMENTAL.

Potassium Salt of 2-Thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole and Iodoform, Bromoform, and Chloroform.

Three molecular proportions of the mercaptide were treated with one molecular proportion of the halogenated compound in alcoholic solution, the mixture being boiled under reflux on the water-bath for several hours. An insoluble mass was obtained consisting of the potassium haloid and the organic derivative. The solution was

allowed to cool and then triturated with water. The aqueous filtrate on evaporation gave crystals of the potassium haloid. The insoluble portion was dried and dissolved in benzene; on evaporation of the solvent, an oily liquid was obtained, which was redissolved in benzene and precipitated by alcohol as an oil. On keeping, the oil solidified to a yellow powder. As it was difficult to get rid of the last trace of iodoform, the powder was repeatedly washed with alcohol and dried in the steam-oven until the odour of iodoform was no longer perceptible. The substance melted at $66-68^{\circ}$.

With bromoform, exactly the same method was followed, but, as it is highly volatile, the excess was easily removed from the yellow compound, which melted at $66-68^{\circ}$.

When the reaction mixture in alcoholic solution was heated at $210-220^{\circ}$ in a sealed tube for several hours, a tarry, resinous mass was obtained, which was collected and dissolved in benzene. Addition of alcohol to the benzene solution gave the same tarry precipitate, but not the yellow powder. The alcoholic mother liquor, on concentration, gave shining, needle-shaped crystals which melted sharply at 62° . Analysis proved this product to be the alcoholate of the compound described above, having the formula $\text{CHR}_3 \cdot 2\text{EtOH}$. The yield was very poor, most of the product having evidently become resinified owing to the high temperature employed. No reaction took place when chloroform was heated under reflux with the mercaptide in alcoholic solution. The mixture was therefore heated in a sealed tube as in the case of bromoform. The filtrate, separated from the resinified mass, gave, on evaporation, crystals of the alcoholate melting at 62° :

0.1520 gave 0.2532 CO_2 . $\text{C}=45.23$.

0.1101 „ 11.4 c.c. N_2 at 32° and 760 mm. $\text{N}=11.26$.

0.1260 „ 0.3532 BaSO_4 . $\text{S}=38.48$.*

$\text{C}_{25}\text{H}_{16}\text{N}_6\text{S}_9 \cdot 2\text{EtOH}$ requires $\text{C}=44.6$; $\text{N}=10.85$; $\text{S}=37.50$ per cent.

It is thus evident that iodoform and bromoform are more reactive towards the mercaptide than is chloroform.

Compound, m. p. $66-68^{\circ}$, from iodoform :

* It may be necessary to point out that in these compounds the sulphur atom is linked both to an aliphatic and to an aromatic and cyclic residue. Carius's method gave an unusually low result, owing to the formation of sulphonic acid. The excess of nitric acid was therefore neutralised with sodium carbonate and evaporated to dryness and fused in a silver dish. The product was evaporated several times with hydrochloric acid before the addition of barium chloride. Owing to the presence of a large amount of sodium chloride and unchanged sodium nitrate, the result is generally a little too high.

0.0953 gave 0.1502 CO_2 and 0.0202 H_2O . $\text{C}=42.98$; $\text{H}=2.33$.
 0.0876 „ 0.2087 BaSO_4 . $\text{S}=41.19$.
 0.075 „ 8.3 c.c. N_2 at 24° and 760 mm. $\text{N}=12.50$.
 $\text{C}_{25}\text{H}_{16}\text{N}_6\text{S}_9$ requires $\text{C}=43.60$; $\text{H}=2.76$; $\text{S}=41.80$; $\text{N}=12.21$
 per cent.

The compound from bromoform gave $\text{C}=43.11$; $\text{H}=2.03$;
 $\text{N}=12.59$ per cent.

Potassium Salt of the Mercaptan and Chloropicrin.

The alcoholic solution of the parent substances was heated at 50° under reflux as before. A bulky, yellow precipitate was obtained; after decanting off the mother liquor, it was washed with alcohol and triturated with water to remove potassium chloride. It crystallised from hot benzene in shining, yellow crystals melting at $128-129^\circ$. The reaction was almost quantitative, as was proved by weighing the potassium chloride formed:

0.1140 gave 0.1727 CO_2 and 0.0307 H_2O . $\text{C}=41.31$; $\text{H}=2.99$.
 0.0948 „ 11.4 c.c. N_2 at 32° and 760 mm. $\text{N}=13.18$.
 $\text{C}_{25}\text{H}_{15}\text{O}_2\text{N}_7\text{S}_9$ requires $\text{C}=40.97$; $\text{H}=2.05$; $\text{N}=13.37$ per cent.

Potassium Salt of the Mercaptan and Tribromoresorcinol.

The substances were heated in alcoholic solution as before. The amorphous powder obtained was freed from potassium bromide by water, dried, and dissolved in a mixture of alcohol and carbon disulphide; on evaporation, shining crystals melting at 166° were obtained:

0.0881 gave 0.1458 CO_2 and 0.0236 H_2O . $\text{C}=45.13$; $\text{H}=2.97$.
 0.0724 „ 0.1897 BaSO_4 . $\text{S}=36.00$.
 $\text{C}_{30}\text{H}_{15}\text{O}_2\text{N}_6\text{S}_9$ requires $\text{C}=46.03$; $\text{H}=2.30$; $\text{S}=36.55$ per cent.

Potassium Salt of the Mercaptan and Benzyldiene Chloride.

The components in alcoholic solution were heated under reflux or about an hour. The crystalline product melted at $59-62^\circ$:

0.0708 gave 0.1321 CO_2 and 0.0193 H_2O . $\text{C}=50.87$; $\text{H}=3.03$.
 0.0849 „ 8.6 c.c. N_2 at 22° and 760 mm. $\text{N}=11.02$.
 0.0974 „ 0.2550 BaSO_4 . $\text{S}=35.83$.
 $\text{C}_{23}\text{H}_{16}\text{N}_4\text{S}_6$ requires $\text{C}=51.11$; $\text{H}=2.96$; $\text{N}=10.40$; $\text{S}=35.55$
 per cent.

Potassium Salt of the Mercaptan and Ethylene Bromide.

After heating in alcoholic solution as usual, the insoluble product was freed from potassium bromide by means of water, dried, and dissolved in ether. On evaporation, shining crystals melting at 94° were obtained:

0.1644 gave 0.2183 CO_2 . $\text{C}=36.21$.

0.0812 „ 6.6 c.c. N_2 at 30° and 760 mm. $\text{N}=8.97$.

0.1303 „ 0.0715 AgBr . $\text{Br}=23.35$.

$\text{C}_{10}\text{H}_9\text{N}_2\text{BrS}_3$ requires $\text{C}=36.03$; $\text{N}=8.40$; $\text{Br}=24.02$ per cent.

Potassium Salt of the Mercaptan and Monochloroacetic Acid.

On mixing the components in aqueous solution, the reaction takes place even in the cold, and is completed on heating. The product crystallises from boiling water in silky needles melting at 145° :

0.1279 gave 0.1935 CO_2 and 0.0414 H_2O . $\text{C}=41.26$; $\text{H}=3.60$.

0.1697 „ 15.00 c.c. N_2 at 24° and 760 mm. $\text{N}=9.99$.

0.1580 „ 0.3495 BaSO_4 . $\text{S}=30.38$.

$\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2\text{S}_3$ requires $\text{C}=42.06$; $\text{H}=2.81$; $\text{N}=9.86$; $\text{S}=33.81$ per cent.

It is of interest to note that whilst monochloroacetic acid behaves in the above manner, dichloro- and trichloro-acetic acids, on the other hand, behave like strong acids, such as hydrochloric acid, that is, they simply regenerate the original mercaptan.

Potassium Salt of 2:5-Dithiol-1:3:4-thiodiazole and Chloropicrin.

The components were heated under reflux in alcoholic solution for several hours. Nitrous fumes were evolved and a yellow precipitate was obtained. On cooling, this was collected and washed with alcohol to remove adhering chloropicrin, and then triturated with water to move potassium chloride. The yellow powder was insoluble in nearly a dozen ordinary solvents and in mixtures of some of them. Two different preparations had, however, the same melting point (166 – 168°) and the same percentage composition:

0.1734 gave 0.1274 CO_2 . $\text{C}=20.04$.

0.0853 „ 14.00 c.c. N_2 at 31° and 760 mm. $\text{N}=18.03$.

0.0899 „ 0.3907 BaSO_4 . $\text{S}=59.68$.

$\text{C}_8\text{ON}_2\text{S}_3$ requires $\text{C}=19.83$; $\text{N}=17.40$; $\text{S}=59.50$ per cent.

CHEMICAL LABORATORY,
COLLEGE OF SCIENCE,
UNIVERSITY OF CALCUTTA.

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CCXII.—*Equilibria Across a Copper Ferrocyanide and an Amyl Alcohol Membrane.*

By FREDERICK GEORGE DONNAN and WILLIAM EDWARD GARNER.

DONNAN and Allmand (T., 1914, 105, 1941) investigated the distribution equilibrium of potassium and chlorine ions across a copper ferrocyanide membrane. In the method adopted, a solution of potassium ferrocyanide was placed on one side of the membrane and a solution of potassium chloride on the other. The results, whilst affording undoubted confirmation of Donnan's theory (*Zeitsch. Elektrochem.*, 1911, 17, 572), were complicated by the uncertainty as to the manner of ionisation of potassium ferrocyanide. It was considered that this difficulty would be overcome if solutions of two ferrocyanides were employed on the two sides of the membrane, especially if these salts were ionised to the same extent. In the present investigation, the sodium, potassium, and calcium salts were found to be suitable, and mixtures of these were used to test the validity of the theory.

With a mixture of sodium and potassium ferrocyanides, equilibrium will be set up by an interchange of sodium and potassium ions, since the membrane is not permeable to ferrocyanogen ions. Assuming that the ions obey the laws of ideal solutions, the equation for the equilibrium is given by

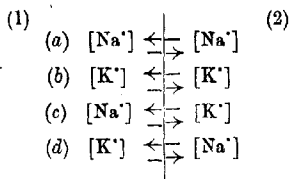
$$[\text{Na}_1'] [\text{K}_2'] = [\text{Na}_2'] [\text{K}_1']$$

where the symbols indicate molar ionic concentrations.

This equation was derived from thermodynamical considerations by Donnan (*loc. cit.*), and its derivation is also possible from the kinetic theory, as follows: The number of ions of any one kind penetrating the membrane is proportional to its ionic concentration, C_1 ; the number of ions exchanging across the membrane is proportional, not only to the concentration, C_1 , but also to the concentration of the ion, C_2 , which interchanges with the first across the membrane, that is,

$$N = K \cdot C_1 \cdot C_2$$

In the case of sodium and potassium ions, at distribution equilibrium four kinds of interchanges across the membrane are possible. Two of these, (a) and (b) (exchange of like ions), do not affect the final concentrations in any way. The four interchanges are shown below:



At equilibrium, the number of exchanges due to (c), that is, $N_c = K[\text{Na}_1^+][\text{K}_2^+]$, must equal that due to (d), that is, $N_d = K[\text{Na}_2^+][\text{K}_1^+]$, therefore $[\text{Na}_1^+][\text{K}_2^+] = [\text{Na}_2^+][\text{K}_1^+]$.

When the calcium salt is substituted for the potassium salt, the equation of equilibrium becomes:

$$(a) [\text{Ca}_1^{++}][\text{Na}_2^+]^2 = [\text{Ca}_2^{++}][\text{Na}_1^+]^2,$$

and

$$(b) [\text{Ca}_1][\text{Na}_2]^2 = [\text{Ca}_2][\text{Na}_1]^2,$$

if the degree of ionisation of the two salts is the same.

In the case of the sodium-potassium cells which were investigated, the experimental results showed good agreement with the requirements of the theory.

The degrees of ionisation of the two salts are very similar, so that the ratio of the molar concentrations of the salts is the same as that of the ionic concentrations.

The sodium-calcium cells, however, gave unexpected results. Whereas the equation (b), which refers to the concentrations of the two salts, holds within the limit of the experimental error of the analysis, it was found that equation (a) above does not accurately represent the relationship between the ionic concentrations of the calcium and sodium salts on the two sides of the membrane. The activities of the ions in this case appear to be more closely related to the molar than to the ionic concentrations. This result also may indicate that adsorption plays an important part in the transference of the ions across the membrane.

Further experiments were carried out in order to find a liquid membrane which would be permeable to one electrolyte and impermeable to a second which contains an ion common to the first. With this purpose in view, the solubilities of several salts in moist, organic solvents were determined. Amyl alcohol was found to be the most satisfactory of these solvents, and potassium and lithium chlorides the most suitable electrolytes. Since lithium chloride is readily soluble in amyl alcohol (a saturated solution is 1.83*N*) and potassium chloride is practically insoluble (a saturated

solution is 0.0048*N*),* it was hoped to set up a cell of the following type:

I. KCl, LiCl in water | Amyl alcohol | LiCl in water II.

which is of the same type as that investigated by Donnan and Allmand with the copper ferrocyanide membrane.

It was not, however, practicable to use an amyl alcohol membrane, owing to the slow rate of diffusion of lithium chloride through the amyl alcohol. The problem was therefore approached in an indirect manner. Determinations were made of the distribution concentrations of lithium chloride between amyl alcohol and water at 25°. Aqueous solutions of lithium chloride and lithium and potassium chlorides were shaken with amyl alcohol, and the two layers separated and analysed. The concentration of the lithium chloride in II, which is in equilibrium with a mixture of the two chlorides in I, was calculated from these results.

The calculation of the ionic concentrations is complicated by the high values of the viscosity of the solutions and by changes in the state of hydration of the lithium ion with concentration. Green (T., 1908, 93, 2023) has deduced the degree of ionisation of concentrated lithium chloride solutions from measurements of the conductivity of solutions of lithium chloride of which the viscosity has been increased by means of sucrose. The chief objection to the values which are obtained in this way lies in the hydration of the lithium ion, which will be affected by the addition of sucrose to the solutions.

The concentrations of the ions and the undissociated part of the electrolyte have, however, been calculated, using Green's values for the degree of ionisation of lithium chloride, and the results are in fairly satisfactory agreement with theory. The agreement is better in those cases where the total concentration of the electrolytes is below 5*N*. Thus $[\text{LiCl}]_1 = [\text{LiCl}]_2$ and

$$[\text{Li}_1'] \cdot [\text{Cl}_1'] = [\text{Li}_2'] \cdot [\text{Cl}_2'].$$

The distribution-coefficient of lithium chloride between amyl alcohol and water has been calculated, and it appears that lithium chloride occurs in amyl alcohol solution as double molecules. The coefficient is, however, only a constant over a small range of concentration, and above 5*N* the coefficient increases. The increase is probably associated with errors in the degree of ionisation due to the dehydration of the lithium ion.

The experimental work in this paper leads to the conclusion that the same equilibrium relationships are established, whether the

* Moist amyl alcohol.

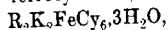
equilibrium is brought about by the transference of ions, as is the case with the copper ferrocyanide membrane, or by the transference of the undissociated part of the electrolyte, as is the case with the amyl alcohol membrane.

EXPERIMENTAL.

The osmometer vessels used in the determination of the ratios of the ions were those described by Donnan and Allmand (T., 1914, 105, 1944). The copper ferrocyanide membrane in parchment paper was clamped in position between two shallow, cylindrical vessels, and was separated from the supporting rim by rubber bands. The vessels, which were of Jena glass, were fitted with side-tubes to facilitate the introduction of the solutions, and the volume of each vessel was about 100 c.c. The membranes were prepared by the method described by Donnan and Allmand (*loc. cit.*), and the parchment paper was usually left in contact with the solutions for two days. The membranes were tested for leaks by placing a ferrocyanide solution on one side and an isotonic solution of sucrose on the other, and no leakage occurred over a period of six weeks.

The ferrocyanides which were used in the investigation were purified by crystallisation from water. The calcium and ammonia ferrocyanides were prepared from hydroferrocyanic acid (Noyes and Johnston, *J. Amer. Chem. Soc.*, 1909, 31, 991).

Since potassium ferrocyanide forms insoluble double salts with magnesium and calcium ferrocyanides, of the type



it was not possible to use potassium ferrocyanide against these salts in the cells. The precipitation of the insoluble salts takes place slowly at the ordinary temperature, but quicker on heating, as if a chemical change were taking place. The double salts with sodium ferrocyanide are soluble in water.

Potassium-Sodium Ferrocyanide Cells.

Solutions were used of a strength 0.025 molar. The usual procedure was to place a solution of potassium ferrocyanide in one side of the cell and a solution of sodium ferrocyanide in the other. The time required for the attainment of equilibrium was determined by conductivity measurements, and no change in the conductivity could be observed after an interval of one week. The cells were, however, allowed to remain, with occasional shaking, over a period of three to five weeks, in which time equilibrium was certain to have been reached.

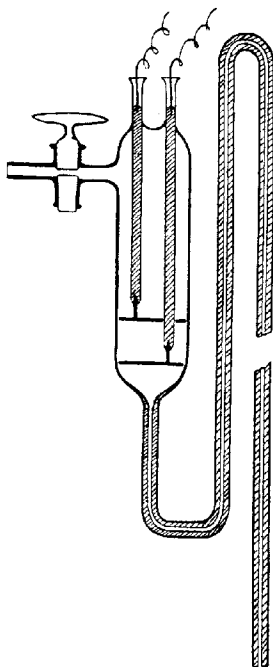
In order to prevent changes in the ferrocyanide solutions with time, several precautions were necessary.

(1) When pieces of well-washed copper ferrocyanide membrane were placed in solutions of ferrocyanides, it was observed that the strength of the solutions diminished several per cent. in three or four days, and at the same time the presence of sulphates in the solutions was detected. The change was almost entirely due to that side of the membrane which was last exposed to the copper sulphate solution. The adsorbed copper sulphate on this side of the membrane reacted with the ferrocyanide solutions, with the formation of sulphates and a slight increase in the thickness of the membrane. The copper ferrocyanide membrane, after being clamped in position, was on this account washed for three to four days with ferrocyanide solutions of the same concentrations as those to be used in the experiment.

(2) Another source of trouble was the oxidation of the ferrocyanides by the small quantity of air enclosed in the osmometer vessels. The oxidation was also considerable if the conductivity of the solutions was measured from time to time in the ordinary conductivity vessels. To make the change due to this cause as small as possible, a special conductivity vessel was constructed (Fig. 1) which could be filled with nitrogen. The amount of air in the osmometer vessel was also reduced to a fraction of a c.c., and in the majority of the experiments, of which the results are given in the tables, the cells were not opened until immediately before analysis.

(3) When solutions of different concentrations were employed on the two sides of the membrane, osmosis of water was prevented by the addition to the solution of the requisite amount of sucrose. The amounts which were added were calculated from conductivity

FIG. 1.



data. The effect due to this cause is, however, small, as Donnan and Allmand have shown (*loc. cit.*).

The solutions were kept in the dark and the cells shaken every two or three days.

Method of Analysis.

The solutions of the ferrocyanides were decomposed with concentrated sulphuric acid, and the sulphates of the alkali metals converted into chlorides by the precipitation of the iron (twice) with ammonia, and of the sulphate with a slight excess of barium chloride. After the removal of the barium as carbonate, the mixed chlorides in the solution were obtained by evaporation and weighed. The potassium was determined as perchlorate and the sodium calculated by difference.

The ferrocyanide concentrations were determined before filling into the cells, and after the equilibrium had been reached, by titration against potassium permanganate solution. These analyses serve as a check on the results obtained by the gravimetric analysis. The variation in the ferrocyanide concentrations as determined by the three methods outlined above rarely exceeded 1 per cent.

A method of analysis based on a conductivity method was not found to give the requisite degree of accuracy.

The results for the potassium-sodium cells are given in table I. The weights of potassium chlorate and the mixed chlorides are given (in order to indicate the possible errors of the analyses), and in columns 6 and 7 are included the molar concentrations of the sodium and potassium on both sides of the membrane *A* and *B*. In column 8 is found the total concentration of the metals, and in 9 and 10 four times the total concentration of ferrocyanogen before and after the experiment. The results show that no large amount of oxidation or absorption of the salts has taken place during the period of the experiment. The ratios of the sodium and the potassium in the solutions on the two sides of the cell are compared in the last column, and it will be observed that the ratio is the same for (*a*) and (*b*) within experimental error. The ratio of the ionic concentrations will be but little different from those given in the table, since the degrees of ionisation of the sodium and potassium ferrocyanides are very similar. The conductivity of 0.025 molar solutions of potassium, sodium, and ammonium ferrocyanides was determined at 25°, and the degree of ionisation calculated. The results are given in table II.

TABLE I.
Potassium and Sodium Ferrocyanide Cells.

Cell No.	Weights of				Normality of				[Na] [K]
	K ₂ CrO ₄	NaCl	KCl	Na	K	Na + K	4Fe(CN) ₆ before.	4Fe(CN) ₆ after.	
1 a.....	0.3123	0.2859	0.1680	0.0325	0.0451	0.0786	0.0794	0.0793	0.743
b.....	0.3145	0.2956	0.1691	0.0410	0.0567	0.0977	0.0995	0.0995	0.723
2 a.....	0.2064	0.1992	0.0881	0.0503	0.0497	0.1000	0.0990	0.0982	1.012
b.....	0.2069	0.1982	0.0869	0.0496	0.0489	0.0994	0.1000	0.0979	0.996
3 a.....	0.1984	0.1973	0.0905	0.0516	0.0477	0.0993	0.1000	0.0998	1.082
b.....	0.2181	0.2181	0.1174	0.0575	0.0524	0.1099	0.1105	0.1095	1.097
4 a.....	0.1839	0.1970	0.0980	0.0559	0.0443	0.1002	0.1001	0.1001	1.262
b.....	0.2163	0.2332	0.1168	0.0666	0.05205	0.1187	0.1199	0.1192	1.280
5 a.....	0.1731	0.1935	0.0931	0.0573	0.0416	0.0989	0.1005	0.0992	1.377
b.....	0.1785	0.1993	0.0960	0.0884	0.0643	0.1527	0.1506	0.1498	1.375

TABLE II.
Degree of Ionisation of Ferrocyanides.

Salt.	$A_{\pm=40}$.	A_{\pm} Kohl- rausch.	100s.
$(\text{NH}_4)_4\text{Fe}(\text{CN})_6$	383.1	742.0	51.6
$(\text{Na})_4\text{Fe}(\text{CN})_6$	337.1	647.6	52.1
$(\text{K})_4\text{Fe}(\text{CN})_6$	393.0*	742.0	52.9

* Noyes.

Thus the relationship given below has been proved to be correct, that is,

$$\frac{[\text{Na}_1]}{[\text{Na}_2]} = \frac{[\text{K}_1]}{[\text{K}_2]}$$

Since the activities of the potassium and sodium ions are probably very similar, the equation deduced by Donnan has been shown to hold.

Sodium-Ammonium Cells.

Ammonium ferrocyanide solutions slowly attack the copper ferrocyanide membrane. The membrane thickens and changes in colour from a dark brown to a reddish-brown. It does not, however, appear to break down, as on one occasion a cell was made up of a solution of ammonium ferrocyanide on the one side and an isotonic sucrose solution on the other. After five weeks, the sucrose solution was tested, and it was found that no ferrocyanide had diffused through the membrane. The concentration of ferrocyanide had, however, diminished, and the colour of the membrane on the one side had changed to a reddish-brown. In consequence of these irregularities, only one sodium-ammonium cell was examined. The ratio $\frac{[\text{Na}]}{[\text{NH}_4]}$ on the two sides were found to be 0.8480 and 0.8595 respectively.

Sodium-Calcium Cells.

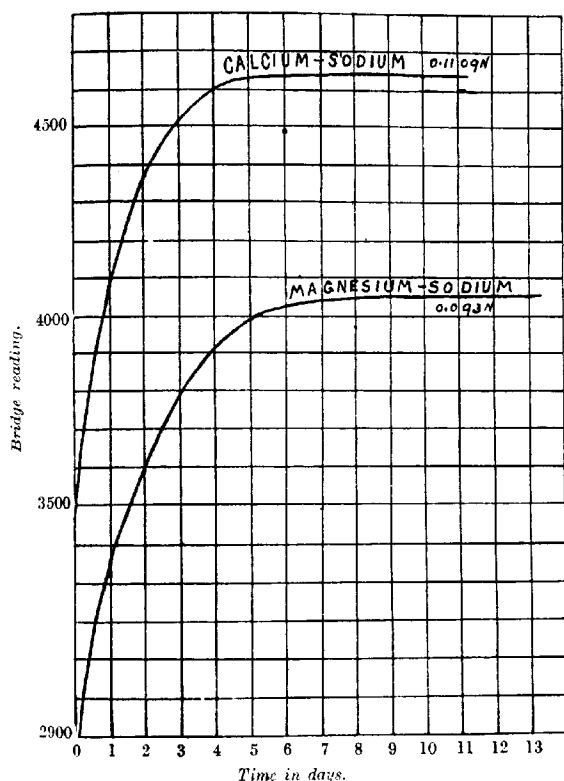
The cells were made up as described previously. The amounts of sucrose used to prevent osmosis were the same as those used with the potassium and sodium solutions of the same concentration. The concentrations of sucrose are probably too great in the case of the calcium solutions, since the calcium salt is less ionised in solution than the potassium salt, but no appreciable osmosis occurred. On the other hand, when the concentrations of sucrose were calculated from Sherrill's equations (*J. Amer. Chem. Soc.*, 1910, **32**, 742), a considerable amount of osmosis occurred.

The rate at which equilibrium is reached is about as rapid as

in the case of the sodium-potassium cells. In some cases, the changes in concentration were followed by conductivity measurements. In Fig. 2 are given the changes of conductivity of a sodium-calcium and a sodium-magnesium cell respectively.

Time in days.	0.	1.	3.	4.	5.	6.	7.	8.	10.	12.
Bridge-reading.										
Na-Ca .	3470	4082	—	4600	—	4635	—	4643	4635	—
Na-Mg .	2974	3358	3800	—	3994	—	4040	—	—	4060

FIG. 2.



From the curves and the above table, it will be readily seen that the rate of exchange of sodium and calcium ions is approxi-

ately equal to that of sodium and magnesium ions, and that a constant reading is obtained in about ten days.

The slight fall in the bridge-reading at the end of the experiment (Na-Ca) is probably due to the oxidation of the ferrocyanide.

Method of Analysis.

The analysis of the solutions of calcium and sodium ferrocyanides gave rise to considerable trouble, owing to the small volume (100 c.c.) which was available for analysis. The ferrocyanide solution was evaporated to dryness and decomposed with concentrated sulphuric acid. The mixed sulphates were dissolved in dilute hydrochloric acid, and the iron was removed as hydroxide with ammonia. The calcium was precipitated as oxalate and converted into oxide. Traces of iron were sometimes present in the oxide, which was on this account dissolved in hydrochloric acid and the iron precipitated. The calcium was then weighed as sulphate. The filtrate containing sodium sulphate was evaporated to dryness, traces of iron were removed, and the sodium was weighed as sulphate.

The results of the analyses are shown in table III, and it is found that

$$\frac{[Ca_1]}{[Ca_2]} = \frac{[Na_1]^2}{[Na_2]^2},$$

where the concentrations represent the total concentrations of the calcium and sodium atoms in the solution.

The ratio of the equilibrium concentrations of the calcium ferrocyanide on the two sides of the membrane is slightly higher than the ratio of the squares of the equilibrium concentrations of the sodium ferrocyanide, but the variations are of the same order as those due to errors of analysis.

The change in the degree of ionisation with concentration is known for potassium and calcium ferrocyanides, but not for sodium ferrocyanide.

	100a K ₄ Fe(CN) ₆	Ca ₄ Fe(CN) ₆
(1) 0.05 Molar	48.6	22.1
(2) 0.025 Molar	53.1	23.5

(Noyes and Johnston, *J. Amer. Chem. Soc.*, 1909, **31**, 1010).

Similar figures have been obtained for calcium ferrocyanide in the course of this work.

Assuming that the sodium salt resembles potassium ferrocyanide, and that the ionisation of the mixed sodium and calcium salts is the same as in solutions of the pure salts with concentrations corre-

TABLE III.
Calcium-Sodium Cells.

Cell.	Weight of		Na.	Normality of $4\text{Fe}(\text{CN})_6$				$\frac{[\text{Ca}_1]}{[\text{Ca}_2]}$	$\frac{[\text{Na}_1]^2}{[\text{Na}_2]^2}$	$\frac{[\text{Na}_1]}{[\text{Na}_2]}$
	CaSO_4	Na_2SO_4		I.	II.	III.	IV.			
1 a.	0.1964	0.2276	0.0573	0.1213	0.1196	0.1185		1.265	1.248	1.117
b.	0.1541	0.2037	0.0453	0.1026	0.1034	0.1029				
2 a.	0.1673	0.2468	0.0615	0.0867	0.1482	0.1495	0.1473	1.762	1.757	1.326
b.	0.1188	0.2324	0.0349	0.0654	0.1003	0.1030	0.1026			
3 a.	0.1478	0.2064	0.0543	0.0726	0.1269	0.1285	0.1236	1.368	1.332	1.154
b.	0.1356	0.2235	0.0397	0.0629	0.1026	0.1049	0.1023			
4 a.	0.1775	0.2537	0.0652	0.0893	0.1545	0.1534	0.1545	1.802	1.775	1.335
b.	0.1231	0.2381	0.0362	0.0670	0.1043	0.1042	0.1032			
5 a.	0.2189	0.1219	0.1287	0.0686	0.1973	0.2140	0.1995	1.547	1.495	1.223
b.	0.2265	0.1595	0.0332	0.0561	0.1393	0.1303	0.1420			

sponding with the ferrocyanogen-ion concentration (Arrhenius), it is possible to calculate the ratios of the calcium-ion concentration and the ratios of the squares of the sodium-ion concentrations on the two sides of the membrane. These are given in the table. The results (table IV) show that the relationship

$$\frac{[\text{Ca}_1^{++}]}{[\text{Ca}_2^{++}]} = \frac{[\text{Na}_1^+]^2}{[\text{Na}_2^+]^2}$$

does not hold so strictly as equation (1).

TABLE IV.
Calcium-Sodium Cells.

No.	$\frac{[\text{Ca}_1]}{[\text{Ca}_2]}$	$\frac{[\text{Na}_1]^2}{[\text{Na}_2]^2}$	$\frac{[\text{Ca}_1^{++}]}{[\text{Ca}_2^{++}]}$	$\frac{[\text{Na}_1^+]^2}{[\text{Na}_2^+]^2}$
1	1.27	1.25	1.25	1.19
2	1.76	1.76	1.68	1.58
3	1.37	1.33	1.33	1.25
4	1.80	1.78	1.73	1.61
5	1.65	1.50	1.49	1.36

The activities of the ions of these two salts thus appear to be more nearly proportional to the molar concentrations than to the ionic concentrations.

Irregularities occurred in two of the cells. Cell 3, which was opened once during the experiment, shows that 2—3 per cent. of oxidation has taken place, and in cell 5 a change, due to osmosis, occurred. Neither of these changes appears to affect the ratio to any great extent.

In cell 5 it should be noted that the concentration of the calcium ferrocyanide is greater than that of the sodium ferrocyanide; in the other cells the reverse is the case.

Amyl Alcohol Membrane.

The results of some preliminary experiments on this membrane are given below.

Materials.—Amyl alcohol (b. p. 131.5°) was obtained by repeated fractionation of fusel oil through a six-bulb fractionating column. One sample of the alcohol was used throughout the work.

The lithium chloride was free from calcium, and was completely soluble in amyl alcohol. Its solution in water was neither acid nor alkaline. It was also analysed by conversion into lithium sulphate, followed by the estimation of the sulphate in this substance, as barium sulphate.

Method.—Aqueous solutions of lithium chloride were shaken with amyl alcohol in stoppered bottles in a thermostat kept at 25°, and when equilibrium had been reached, the two layers were analysed.

Analysis.—The aqueous solutions of lithium chloride were estimated volumetrically with *N*/10-silver nitrate, and the results were checked by analysis of the lithium as sulphate.

A known volume of the amyl alcohol layer was placed in a Jena-glass distilling flask, and the amyl alcohol distilled off. Water was added to the residue, and the solution titrated with silver nitrate.

The solutions containing the potassium and lithium chlorides were analysed according to the method employed by Gooch (*Proc. Amer. Acad.*, 22 N.S. 14, 177). A known volume of the aqueous solution was evaporated in the presence of 10 c.c. of amyl alcohol, and a little hydrochloric acid added to convert any lithium hydroxide into chloride. The lithium chloride dissolves in the amyl alcohol, and potassium chloride is left behind. The residue is collected and washed with hot amyl alcohol. The lithium is then estimated as sulphate, and the potassium chloride dissolved in water and estimated with silver nitrate. To check the results, the solution of the mixed chlorides was titrated directly with silver nitrate.

Results.—The concentrations of lithium chloride in the two layers are given in table V. The concentration of the lithium chloride in amyl alcohol diminishes rapidly with decrease in the concentration in the aqueous solution. The degree of ionisation of lithium chloride solutions cannot be given with any accuracy. The viscosity of the solutions is so great that allowance must be made in the derivation of the degree of ionisation from the conductivity results. Green (*loc. cit.*) has determined the

TABLE V.
*Distribution of Lithium Chloride between Amyl Alcohol and Water.**

$\text{LiCl}_{\text{Aq.}}$ Total.	$[\text{LiCl}]_{\text{Am.}}$ Total.	100a.	$[\text{LiCl}]_{\text{Aq.}}$ undissociated.	$\frac{[\text{LiCl}]_{\text{Am.}}}{[\text{LiCl}]_{\text{Aq.}}}$
12.54 <i>N</i>	1.735 <i>N</i>	36.9	7.91 <i>N</i>	0.0273
8.49	0.903	47.8	4.43	0.0428
7.77	0.683	50.5	3.85	0.0418
6.68	0.387	54.2	3.06	0.0366
5.00	0.1266	60.1	2.00	0.0277
3.14	0.0342	66.3	1.06	0.0255
3.00	0.0314	66.7	1.00	0.0262
2.71	0.0251	67.7	0.88	0.0268

* In the calculation of the equilibrium constant a correction has been made for the degree of ionisation of the LiCl in the amyl alcohol solution.

viscosity and conductivity of solutions of lithium chloride over a wide range of concentration, and has corrected for the effect of viscosity by the addition of sucrose to the solution. The conductivity at infinite dilution was calculated over a wide range of viscosities; the degree of ionisation is obtained directly from the equation $\alpha = \frac{\Lambda}{\Lambda_f}$, where Λ is the conductivity of a solution of lithium chloride and Λ_f the conductivity at infinite dilution of a solution of lithium chloride containing sucrose, and with the same viscosity as the first solution. Washburn (*J. Amer. Chem. Soc.*, 1911, 33, 1461) finds that the relation between the degree of ionisation, the conductivity, and the viscosity is given by the relation $\alpha = \frac{\Lambda}{\Lambda_0} \left(\frac{f_0}{f} \right)^m$, where f represents the fluidities and $m=0.94$, but this holds only from 0—1.0*N*. For more concentrated solutions, m varies with the concentration. In table VI, m is given for the concentrations

TABLE VI.

Degree of Ionisation of Concentrated Lithium Chloride Solutions.

Normality.	f .	m .	λ .	$100 \frac{\Lambda}{\Lambda_0} \left(\frac{f_0}{f} \right)^m$	$100\alpha(\text{Green})$.
0.0	111.67	—	115.3	—	—
2.0	84.87	0.900	61.63	68.4	69.9
3.0	73.64	0.858	52.58	65.2	66.7
4.0	63.65	0.832	44.76	61.9	63.5
5.0	54.59	0.812	37.85	58.7	60.1
6.0	46.27	0.798	31.70	55.5	56.8
7.0	38.60	0.785	26.04	52.0	53.1
8.0	31.55	0.771	21.05	48.4	49.5
9.0	25.28	0.759	16.725	44.8	46.0
10.0	19.75	0.749	13.225	42.0	43.1
11.0	15.07	0.738	10.395	39.5	40.6
12.0	11.42	0.729	8.149	37.2	38.2

2—12*N*, and the value of m decreases from 0.90 to 0.73. The degree of ionisation calculated from the above equation and the data given by Green will be found in columns 5 and 6. The values are the same as those obtained by Green to within 1—2 per cent. The method of calculation is open to the objection that the lithium ion is probably hydrated in solution, and that the conductivity at infinite dilution, Λ_0 , is given by lithium ions, which are probably hydrated to a different extent than is the case in a pure solution of lithium chloride with the same viscosity. The calculated values of the degree of ionisation will therefore be the more accurate for the more dilute solutions.

The values of α in table VI, column 6, are used in tables V and VII. In table V, the amount of undissociated lithium

chloride (column 4) is calculated from these values of α . From the figures in the last column, it will be seen that lithium chloride is associated in amyl alcohol solution to double molecules. A constant for $\frac{[\text{LiCl}]_{\text{Am.}}}{[\text{LiCl}]_{\text{Aq.}}}$ is only obtained between $2N$ and $5N$.

Above this concentration, the coefficient rises from 0.0277 to 0.0428, and then falls. The most probable cause of this deviation is discussed above, and it appears that the calculated concentrations of the undissociated molecules are too low.

The molar concentrations of the solutions of mixed chlorides in I. (p. 1315) and the corresponding equilibrium concentrations of lithium chloride in the amyl alcohol are given in table VII.

TABLE VII.

Results with Amyl Alcohol Membrane.

No.	Total KCl.	Total LiCl.	LiCl in amyl alcohol.	Total LiCl.	Undissociated LiCl		[Li'] \times [Cl']	
	I.	I.		II.	I.	II.	I.	II.
1	0.944	3.504	0.554	3.78	1.44	1.36	5.94	5.86
2	1.200	2.613	0.303	2.95	0.945	0.976	4.045	3.900
3	0.962	5.45	0.2236	5.80	2.39	2.46	11.02	11.17

From the amount of salt dissolved by the amyl alcohol, and the data in table V, the corresponding values of lithium chloride in II. are calculated and given in column 5. These figures represent the concentrations of lithium chloride in equilibrium with the solution of mixed chlorides in columns 1 and 2 across the amyl alcohol membrane. The ionic concentrations are obtained from Green's values for lithium chloride and from Kohlrausch and Grotrian's values for potassium chloride. The degree of ionisation for the higher concentrations of potassium chloride are obtained by extrapolation from the latter values. The degrees of ionisation of lithium and potassium chlorides are apparently very similar. The ionic concentrations of the solutions of the mixed chlorides are calculated on the assumption made in the case of the calcium-sodium ferrocyanide cells.

Cells 1, 2, and 3 show good agreement with the equations $[\text{LiCl}]_1 = [\text{LiCl}]_2$ and $[\text{Li}']_1 [\text{Cl}_1'] = [\text{Li}']_2 [\text{Cl}_2']$. The agreement, which is better than would be expected, supports the values for the degree of ionisation of lithium chloride which were obtained by Green.

Summary.

Determinations have been made of the equilibrium concentrations of solutions of sodium and potassium ferrocyanides and

sodium and calcium ferrocyanides across a copper ferrocyanide membrane, and the results are in general agreement with Donnan's theory.

The following cells were investigated:

(a) I. Potassium ferrocyanide	Sodium ferrocyanide	II.
(b) I. Sodium ferrocyanide	Calcium ferrocyanide	II.
(c) I. Sodium ferrocyanide	Ammonium ferrocyanide	II.

The solutions in (a), (b), and (c) were in the neighbourhood of 0.025*N*.

A liquid membrane has been investigated; amyl alcohol was chosen as the most suitable solvent, and the electrolytes employed were potassium and lithium chlorides.

(d) I. Lithium chloride	Amyl alcohol	Lithium chloride	II.
Potassium chloride			

Lithium chloride gives rise to double molecules in amyl alcohol solution, and a constant is obtained for the partition-coefficient up to 5*N*.

So far as the preliminary experiments go, the equilibrium concentrations of the lithium and chlorine ions and the undissociated part of the electrolyte agree with Donnan's theory.

UNIVERSITY COLLEGE,
GOWER STREET,
W.C. 1.

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CXXIII.—*The Colouring Matter of the Red Pea Gall.*

By MAXIMILIAN NIERENSTEIN.

THE colours of oak galls are very varied and rich. They range from white and cream through all tints of yellow to deep orange, from pale green to a rich, dark hue, and through almost every shade of red, some being very beautiful and attractive. These red colours are generally ascribed to the presence of anthocyanins, which are supposed to be derived from the tannins present in galls (compare Gertz, "Studien öfver Anthocyans," 1906; Connold, "British Oak Galls," 1908; Küster, "Die Gallen der Pflanzen," 1911; Magnus, "Die Entstehung der Pflanzengallen," 1914). Our knowledge of the anthocyanins has been fundamentally increased

by the recent investigations of Wheldale, Willstätter, Everest, and others (compare Perkin and Everest, "The Natural Organic Colouring Matters," 1918). Their researches have conclusively proved that the anthocyanins are derived from the different flavones present in plants. This suggested an inquiry into the colouring matter of the so-called anthocyanin of the "red pea gall," frequently found on the leaves of different British oak trees, especially *Quercus pedunculata* when galled by *Dryophanta divisa*, Adler. It seemed reasonable to expect that the anthocyanin of this gall would in all probability be derived from cyanidin, the anthocyanin of quercetin, and, if so, it might furnish some evidence regarding the much discussed question as to the relationship between the pathological products produced by the gall and those normally present in the plant (compare Dekker, "Die Gerbstoffe," 1913). It was, incidentally, also thought possible that an anthocyanin derived from a gall might prove to be closely allied to quercetone or isoquercetone, both anthocyanin-like oxidation products of quercetin, described by Nierenstein and Wheldale (*Ber.*, 1911, **44**, 3487) and Nierenstein (*T.*, 1915, **107**, 869; 1917, **111**, 4), as it was probable that the accelerated oxidative processes common to larvæ and imagines (compare Krogh, "The Respiratory Exchanges of Animals and Man," 1916), which, in addition to numerous inquilines, are present in large numbers in galls (compare Connold, *loc. cit.*; Küster, *loc. cit.*), would favour the production of an oxidation product, such as quercetone, and not that of a reduction product, such as cyanidin (compare Everest, *Proc. Roy. Soc.*, 1914, [*B*], **87**, 444).

The investigation of the red colouring matter derived from the "red pea gall" has, however, to some extent proved disappointing. It was found that *dryophantin*, the name suggested for this pigment, was in no way allied either to the flavones or to the anthocyanins, but that it consisted of purpurogallin and two molecules of dextrose. On the other hand, it must be mentioned that purpurogallin has not previously been found in nature. *Dryophantin* is derived from pyrogallol, like gallotannin, and is therefore of pathological origin, like the latter. *Dryophantin*, however, cannot be regarded as an anthocyanin, and probably the same can be said of the other so-called anthocyanins derived from plant galls. It is therefore proposed to classify these red pigments in a new group of natural organic colouring matters, to which the name *gallorubrones* is assigned.

Preparation of Dryophantin.

The galls used in this investigation were collected in the vicinity of Bristol and East London during the months of August and September, 1913, 1915, 1917, and 1918, and care was taken to avoid admixtures with the different galls of the *Neuroterus* species frequently met with on the same leaves as the galls of *Dryophanta divisa*. In all, 94 grams of the galls were collected, and the dried material was powdered and extracted in a Soxhlet apparatus, at first with ether and subsequently with chloroform, so as to remove wax, chlorophyll, and the so-called gall-fats. The carefully dried powder was then again extracted in a Soxhlet apparatus with alcohol, which dissolved both the colouring matter and the tannins. The alcohol was distilled off in a vacuum, and the viscid residue redissolved in water. The cold aqueous solution, made up to 150 c.c., was shaken with 5 grams of fat-free caseinogen to remove the tannins (compare Körner and Nierenstein, *Chem. Zeit.*, 1911, 36, 31), filtered, and extracted with ether. The ether left on evaporation only traces of a tarry substance, apparently a by-product. The aqueous solution was evaporated under diminished pressure at about 55° (water-bath temperature), and the residue dissolved in boiling alcohol and filtered. The red alcoholic extract, after being evaporated to a small bulk, was poured into water, the mixture extracted several times with ether, and the small quantities of alcohol and ether present were removed from the aqueous liquid by prolonged heating on a boiling-water bath. The solution, on cooling, became semi-solid, owing to the separation of crystals; these were collected and washed repeatedly with ether and dilute alcohol. The deep red product obtained in this way was purified by several crystallisations from dilute, and finally absolute, alcohol. The air-dry substance was dried at 130° for analysis, without apparent loss of weight. The total amount of dryophantin thus obtained corresponded with about 4 grams, and there was no apparent difference if fresh or old material (about six months old) was used, which showed that there was apparently no deterioration on keeping.

Found: C=50.2, 50.4; H=5.5, 5.4.

$C_{23}H_{23}O_{15}$ requires C=50.6; H=5.2 per cent.

Dryophantin was obtained in deep red, glistening needles with a bronzy lustre. It was almost insoluble in cold alcohol, sparingly soluble in hot water, but fairly readily so in boiling methyl and ethyl alcohol, and in larger quantities of boiling acetone. It sintered at 216° and melted at 219–220° to a viscous liquid. The

addition of ferric chloride to its alcoholic solution produced a brick-red precipitate, and a similar precipitate, but slightly darker in colour, was also obtained by the addition of lead acetate. A trace of ammonia turned the alcoholic solution deep blue, which became red on acidification. These colour changes could be produced in an unlimited number of times in the same solution without affecting its sensitiveness to these reagents. Similar blue solutions were also obtained by the addition of sodium, potassium, or barium hydroxides to alcoholic solutions of dryophantoin. In this connexion, it must be mentioned that similar colour changes are also given by purpurogallin itself (compare Wichelhaus, *Ber.*, 1872, **5**, 848; Struve, *Annalen*, 1872, **163**, 164; Hooker, *Ber.*, 1887, **20**, 3259). On repeating these observations, it was found, however, that the colour changes are not so permanent in the case of purpurogallin as in the case of dryophantoin.

Hydrolysis of Dryophantoin.

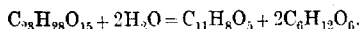
Experiments having shown that dryophantoin was a glucoside, its decomposition with acid was studied in the following manner.

0.5246 Gram, dissolved in 550 c.c. of boiling water, was digested with 5 c.c. of sulphuric acid for two hours. A deep red, crystalline product commenced to separate, and more of it was deposited on cooling. This was collected in a Gooch crucible, washed with cold water so as to remove all traces of sulphuric acid, and dried at 160°. In this way, 0.1928 gram of purpurogallin was obtained.

Found: Purpurogallin = 36.7.

$C_{23}H_{28}O_{15}$ requires purpurogallin = 40.4 per cent.

The low value obtained for purpurogallin is due to its sparing solubility in water, and it was found that the filtrate recovered on hydrolysis of dryophantoin to which had been added the washings of purpurogallin contained 2.2 per cent. of purpurogallin, when determined colorimetrically by Willstätter and Stoll's method for the estimation of small amounts of purpurogallin (*Annalen*, 1918, **416**, 46). The total amount of purpurogallin from dryophantoin corresponded, therefore, with 38.9 per cent., which is 1.5 per cent. below the theoretical if the hydrolysis of dryophantoin is expressed as:



A second experiment gave 37.1 per cent. of purpurogallin gravimetrically and 1.9 per cent. colorimetrically, corresponding with 39.0 per cent. of purpurogallin, which is 1.4 per cent. below the theoretical.

The purpurogallin recovered from dryophantin was recrystallised from glacial acetic acid, and had the correct melting point of $274-275^{\circ}$ generally given for purpurogallin (Found: $C=59.8$; $H=3.7$. Calc.: $C=60.0$; $H=3.6$ per cent.). The acetyl derivative, which had been prepared by digesting with acetic anhydride, crystallised from alcohol in orange-yellow needles melting at $179-180^{\circ}$, and the melting point was not depressed after mixing with the tetra-acetyl derivative of purpurogallin (Found: $C=59.2$; $H=4.7$. Calc.: $C=58.7$; $H=4.1$ per cent.).

The filtrate from the first hydrolysis was quantitatively tested for dextrose by Fischer and Freudenberg's method (*Ber.*, 1912, 45, 915), and the dextrose estimated volumetrically in several portions of the hydrolysate by Bertrand's method (*Bull. Soc. chim.*, 1906, [iii], 35, 1286), as used by Geake and Nierenstein (*Ber.*, 1914, 47, 893) for the estimation of dextrose in gallotannin.

Found: Dextrose = 62.8, 63.1, 63.0.

$C_{23}H_{28}O_{15}$ requires dextrose = 63.3 per cent.

The filtrate of the second hydrolysis was prepared as in the experiment for the quantitative estimation of dextrose, and then concentrated to a small bulk. It was subsequently converted into dextrosazone, which crystallised from dilute alcohol in glistening, yellow needles melting at $203-204^{\circ}$ (Found: $N=15.8$. Calc.: $N=15.6$ per cent.).

The author begs to acknowledge his indebtedness to the Government Grant Committee of the Royal Society for a grant from which much of the cost of the investigation was defrayed.

BIO-CHEMICAL LABORATORY,
CHEMICAL DEPARTMENT,
UNIVERSITY OF BRISTOL.

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CXXIV.—*The Effect of Salts on the Vapour Pressure and Degree of Dissociation of Acetic Acid in Solution. An Experimental Refutation of the Hypothesis that Neutral Salts Increase the Dissociation Constants of Weak Acids and Bases.*

By JAMES WILLIAM MCBAIN and JAMES KAM.

IN 1899 Arrhenius proposed a modification of his classical dissociation theory to the effect that salts increase the dissociation

constants of weak acids present with them in solution, as if either the water had acquired greater dissociating power or the salt itself was acting as a dissociating medium. The experimental evidence he adduced was the rate of inversion of sucrose by weak acids in the presence of salts.

Arrhenius's idea was very generally accepted and developed, particularly in the field of non-aqueous solutions; but in 1914 it was called in question by McBain and Coleman's re-interpretation of the direct experimental evidence. On recalculation of the data given by Arrhenius, in conformity with present-day conceptions of this reaction, they found that the supposed effect was entirely absent, thus reversing the significance of the experiments. In other words, the dissociation constant of weak acids is not affected by the presence of salts.

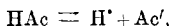
They followed this up by a review of all the available experimental evidence bearing on this subject, and they found that it supported only the simple form of the classical dissociation theory.

One isolated group of experiments was left outstanding, inasmuch as in this particular case the measurements were conflicting in their evidence; these were certain determinations of hydrogen ions by the method of electromotive force. The potential of the hydrogen electrode in solutions of acetic acid was greater than that predicted when sodium chloride was present, although this was not the case when sodium acetate was the added salt.

(1) *Object of the Present Investigation.*

The present communication adduces a hitherto unsuspected but general effect of such salts as sodium chloride on undissociated acetic acid, which would account for the apparent results derived from the measurements of hydrogen electrode potential.

The equilibrium under discussion is



where HAc stands for a weak acid such as acetic acid. The potential of the hydrogen electrode in this solution is admittedly too great when sodium chloride is present. This has hitherto been interpreted as a real increase in acidity; in other words, a displacement of the equilibrium to the right—an enhancement of the dissociation constant itself.

The electrical potential of the hydrogen electrode, however, measures the product of the chemical potential and the concentration of the hydrogen ion. Instead of assuming that the increase in this product is due to increase in concentration, we here submit

experimental evidence for the alternative explanation that the other factor, the chemical potential, has been enhanced.

If the concentration of the hydrogen ion has remained unaltered, but its chemical potential or reactivity has been increased, it is necessary for the continuance of equilibrium that the chemical potential or reactivity of the substance on the left-hand side of the chemical equation should likewise have increased. Such increase in reactivity or potential of undissociated acetic acid in the solution must be accompanied by a parallel increase in the partial pressure of acetic acid in the vapour phase.

This is open to direct experimental test, and we find that a remarkable increase is actually exhibited, fully accounting for the electromotive force data observed. This removes the last evidence in favour of Arrhenius's proposed modification of his classical dissociation theory. The effect here discovered has to be taken into account in most determinations of electromotive force.

(2) *The Experimental Method.*

The simple experimental method adopted was the distillation of aqueous solutions of acetic acid with and without addition of various salts.

Pipettes, burettes, and measuring flasks were carefully calibrated. The distillations were carried out in a flask of fused silica of about 1500 c.c. capacity, heated directly by contact with a large Bunsen flame. The neck and upper half of the flask were covered with a lagging of magnesia and asbestos, so as to avoid as much as possible fractional distillation in the flask. The distance between burner and flask was kept constant through all distillations, as was also the flame itself.

The quantity of distilling liquid was each time 1000 c.c., and the distillate was collected in four to five fractions of about 75 c.c. each. After each fraction, the distillation was quickly interrupted for the abstraction of a similar quantity of about 75 c.c. from the residue in the flask; the first residue was abstracted as soon as the liquid began to boil and just previous to the collection of the first fraction of the distillate.

The residues were left to cool in glass-stoppered bottles, vaseline being used on the stoppers to prevent ingress of carbon dioxide from the air.

Samples of 20 c.c. of each of the distillates and residues were titrated against standard solutions of sodium hydroxide of approximately equal strength, with phenolphthalein as indicator; the usual precautions were taken to avoid the vitiating effect of carbonic acid. Thus for each distillate the ratio R_2 could be

determined between the concentrations of acetic acid in that distillate and the mean concentration of acid in the residue in the flask before and after.

Thus the ratio R_2 was determined for solutions of acetic acid of concentrations varying from 0.05 to 0.5*N*. It appeared that, at least between these limits, R_2 increases only very slightly with the concentration, as is apparent from the curve No. I of Fig. 1, which shows the value of R_2 plotted against the acid concentrations.

The same operations were repeated with solutions of sodium, potassium, and lithium chlorides, potassium thiocyanate, potassium nitrate, sodium sulphate, and sodium acetate in 0.05 to 0.4*N*-solutions of acetic acid. The concentration of the salts was determined by careful evaporation of 20 c.c. of each residue in a porcelain evaporating dish in a hot-air oven at temperatures depending on the nature of the salt in question. The acetic acid was titrated as before, in distillate and residue, to obtain the ratio R_1 of the concentration.

The values of the ratios R_1 are dependent on the concentration of the salts, but they are independent of the concentration of acetic acid. Sodium acetate differs from the other salts investigated in that it has scarcely any effect on the distillation of acetic acid.

In this manner, values of R_2 derived from a very large number of distillations of solutions of pure acetic acid became the standard of comparison for a number of distillations of acetic acid containing added salts.

The expression $100 \frac{(R_1 - R_2)}{R_2}$ gives the percentage increase of the ratio R_1 caused by the addition of salt. The experimental data here presented comprise well above one hundred such determinations.

(3) *Method of Calculation of the Distillation Data.*

Distillation was selected for the measurement of the partial vapour pressure of acetic acid merely for the sake of convenience and accuracy. It must be borne in mind that the composition of the distillate shows only the relative proportion of acetic acid and water vapour in the vapour phase above the solution. What is required is the absolute magnitude of the partial vapour pressure of acetic acid at a definite temperature, say 100°. The polymerisation of the acetic acid vapour may be neglected for the present purpose, since it amounts to only a few per cent. at these low

partial pressures. Even this slight effect is largely eliminated in comparing R_1 with R_2 .

Ordinary variations in barometric pressure and the concomitant alterations in boiling point have no appreciable influence on the composition of the distillate. Hence, all the distillations may without error be regarded as having been in effect carried out at 100°, even where much salt has been added.

In order to obtain the absolute instead of the relative magnitude of the partial pressure of acetic acid in the vapour distilling over at 100°, the actual partial pressure of the water has to be evaluated. Now, the partial pressure of the water, which in pure water was 760 mm., has been diminished by two effects, for which allowance has to be made.

The first correction may be termed the "osmotic correction." The vapour pressure of the solvent has been reduced in familiar fashion through the osmotic activity of the substance in solution. Hence, in all cases the observed concentration of the acetic acid in the distillate must be diminished accordingly before use. This is readily done with sufficient accuracy for the present purpose by taking the lowering of vapour pressure of the solvent to be 1.80 per cent. per mol. of total solute (ions and undissociated acid and salt).

The second correction is the "volatility correction." It results from the effect of the appreciable partial pressure of the acetic acid in lowering the pressure at which the water actually distills over, instead of this occurring at a partial pressure of water vapour equal to 760 mm. Here again, then, in order to base the relative magnitude of the partial pressure of acetic acid on the constant value of 760 mm. for that of water vapour throughout, the volatility correction has to be applied so as to diminish the observed concentration of the acetic acid in the distillate accordingly. This consists in the reduction of the latter by 0.12 per cent. for a 0.1*N*-solution of acetic acid, and taking this correction as proportional to the concentration of the acetic acid in the distillate. Since the acetic acid was at most $N/2$, this correction in no case exceeded 0.6 per cent.

A third and final correction had to be made, this time in the apparent composition of the solution undergoing distillation. This is the "correction for dissociation" of the acetic acid in the solution. The actual ratios measured were those between the concentrations of distillates and the corresponding solutions in the distilling flask (the "residues"). What is required is the ratio based on the actual concentration of undissociated acetic acid in the flask. In the case of solutions containing only acetic acid,

this consisted simply in subtracting the known amount of dissociated acetic acid from the total concentration of acetic acid in the flask. The dissociation constant of acetic acid was taken to be 1.11×10^{-5} at 100° .

The correction for dissociation involves much calculation where salt is present, since in order to determine the actual concentration of undissociated acetic acid, it is necessary to calculate the amounts of the various ions and undissociated salts present, including those formed by metathesis. For example, with common salt the following molecular species were present: H^+ , Ac^+ , Na^+ , Cl^- , HAc , HCl , $NaCl$, and $NaAc$.

This was done by Arrhenius's method, which is based on the principle of isohydrism (*loc. cit.*), and agrees with the method of Sherrill (*J. Amer. Chem. Soc.*, 1910, **32**, 741). The calculation is laborious and involves successive approximations. Fortunately, the exact degree of dissociation of the various salts has but little influence on the results, since the really important values appear in both numerator and denominator of Arrhenius's equations; conductivity data at the ordinary temperature could therefore be employed failing the existence of such at higher temperatures and concentrations. Indeed, the calculation for solutions of one salt in acetic acid might have been applied to the case of any other salt of the same concentrations, except, of course, in the case of sodium acetate. The effect is chiefly dependent on the relative concentration of acid and added salts.

(4) *The Distillation of Solutions of Pure Acetic Acid.*

Following the method already described, fifteen distillations were carried out with $N/20$ - to $N/2$ -solutions of acetic acid involving more than seventy determinations. The object in view was to determine the ratio R_2 , that is, the ratio, concentration of acid in distillate to concentration of acid in residue.

$$\text{Thus} \quad R_2 = \frac{C_d}{C_r},$$

C_d being the concentration of the distillate, C_r being the mean value of the concentrations of the residue before and after the separation of the distillate.

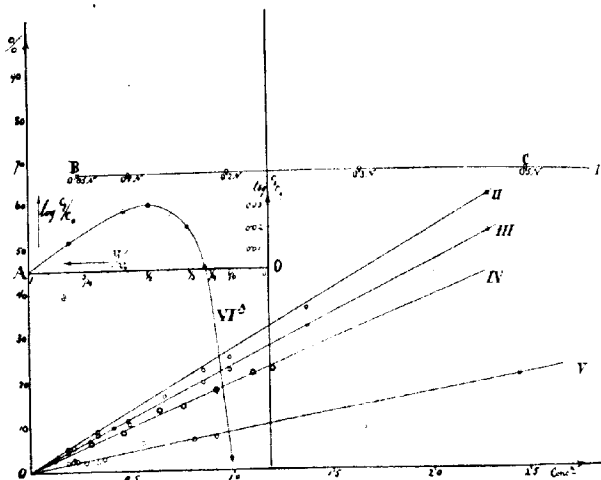
The experimental evidence is summarised in table I. For any one concentration, the results agreed to within 1 per cent. The values of R_2 were corrected as described in Section (3) above, and they increase by only about 1 per cent. over the whole range of concentration. The relative concentration of double molecules, which has not been allowed for, changes from about 5 to 3 per cent. over this same range.

*Ratio of Concentration in Distillate and Residues in Aqueous
Acetic Acid.*

Concentration of acid in flask.	R_2 (uncorrected).	R_2 (corrected).
$N/20$	0.662	0.671
$N/10$	0.666	0.671
$N/5$	0.673	0.674
$N/3$	0.680	0.677
$N/2$	0.685	0.678

The corrected values of R_g increase very slowly indeed. Plotting them against the concentrations, we obtain a straight line (Curve I in Fig. 1).

FIG. 1.



I. $\text{CH}_3\cdot\text{CO}_2\text{H}$, corr. (B = 0.671; C = 0.678).
 II. NaCl, uncorr. Percentage increase due to salt.
 III. NaCl, corr. " " " "
 IV. KCl, " " " "
 V. KCNS, " " " "
 VI. Curve: $\log \frac{C_1}{C_0} = \frac{1}{2.3026} \left[(1 - R_2) \cdot \log \frac{v_0}{v_1} + 2.3026 + R_2 \cdot K \cdot \left(\frac{v_1 - v}{v_1 \cdot v_0} \right) \right]$
 $\Delta 0 = v_0 = 1.$

Ratios of acetic acid in distillate and residue with and without added salts.

The corrections for volatility and osmotic effect can be taken from graphs; for example, in the case of *N*/20-acetic acid, they

amount to -0.06 and -0.09 per cent. respectively. The third correction for degree of dissociation of the acetic acid is here 1.50 per cent. Thus the total correction in this case is an increase of 1.35 per cent. on the observed ratio $R_2=0.662$. Hence we obtain

$$R_2 \text{ (corrected)} = 0.662 \times 1.0135 = 0.671.$$

This value is smaller than the one arrived at by Lord Rayleigh (*Phil. Mag.*, 1902, [vi], 4, 535), $R_2=0.73$. Corrected, it reduces slightly to 0.725 , which is still considerably greater (the reduction in this case being caused by the method of calculation of R_2 from the residues). The discrepancy is, however, probably due to the different manner of heating. Lord Rayleigh kept the neck and upper part of the distilling flask hotter than the boiling liquid in order to prevent condensation. We found, however, that this involved the quantitative evaporation of drops splashing up from the boiling liquid, which produces the same error as if they had splashed directly into the distillate. It was for this reason that we relied on good heat insulation and fairly rapid distillation.

Note on the Calculation of the Composition of the Residues at any given Stage of the Distillation of Acetic Acid.

Following Lord Rayleigh (*loc. cit.*), but using concentration of residues expressed in mols. per litre,

$$\frac{C_0}{C_1} = \left(\frac{V_0}{V_1} \right) R_2 - 1,$$

where C_0 and C_1 are the concentrations and V_0 and V_1 the volumes in the distilling flask before and after the distillation.

For example, for $R_2=0.671$ and $\frac{C_0}{C_1} = \frac{1}{2}$, $\frac{V_0}{V_1} = 8.221$. Hence, in order to double the concentration of the residual acid solution in the flask, $\frac{7.221}{8.221} = 0.878$, or almost 88 per cent. of the volume of the

solution must be distilled over. For $R_2=0.73$ (Rayleigh's value in $N/10$ -solution), this quantity would amount to 92 per cent.

Again, if 40 per cent. of the original volume of solution is distilled off, that is, if $V_1=0.6 V_0$, $\frac{C_1}{C_0} = 1.183$, which means that the concentration of the residue will have increased by 18.3 per cent.

(5) *The Experimental Data for Added Salts.*

Having determined the ratios R_2 for solutions of acetic acid, the corresponding ratios, R_1 , were obtained in exactly the same manner, but with a salt added to the solution.

The salts used were the purest obtainable in 1913, and are named in Section (2) (above).

The distillates were in each case tested for traces of the stronger acid formed by metathesis, but these were found to be negligible. The corrections were calculated and applied in the same manner as before, except that the acetic acid destroyed by metathesis was calculated according to Arrhenius's principle of isohydrium (*Zeitsch. physikal. Chem.*, 1899, **30**, 208).

The results are summarised in tables II—VIII, which require no further explanation, except to note that in tables II and VII space is saved by averaging the figures for all the values obtained over certain ranges of concentration. The number of experimental values so averaged is given in the last column.

With the exception of sodium acetate, all these salts cause a remarkable increase of the ratio $\frac{C_d}{C_r}$, and sodium chloride shows this increase more than any other of the salts investigated. Sodium acetate, on the other hand, appears to have no appreciable effect even in 1.0*N*-solution.

TABLES II.—VIII.

Ratios R_1 of Concentration of Distillates and Residues of Aqueous Acetic Acid with added Salts, and Increase thereof over R_2 of Table I.

TABLE II. (Curves II. and III.). *Sodium Chloride.*

HAc.	Salt.	R_1 .	R_2 .	R_1 (corr.).	R_2 (corr.).	$100 \left[\frac{R_1 - R_2}{R_2} \right]$	Expts.
0.1—0.2	(0.12)	0.688	0.669	0.690	0.673	2.6	7
0.1—0.3	(0.21)	0.708	0.671	0.710	0.673	5.4	16
0.1—0.3	(0.29)	0.721	0.672	0.716	0.673	6.6	15
0.1—0.3	(0.41)	0.742	0.671	0.721	0.673	9.6	4
0.13	0.661	0.790	0.668	0.715	0.671	16.9	1
0.076	1.04	0.830	0.663	0.820	0.671	22.2	1
0.078	1.38	0.904	0.664	0.885	0.671	32.1	1
0.077	2.30	1.076	0.664	1.033	0.671	53.9	1

TABLE III. (Curve IV., Fig. 1). *Potassium Chloride.*

0.22	0.2—0.3	0.7146	0.673	0.7111	0.674	5.55	4
0.2540	0.4673	0.7389	0.675	0.7309	0.675	8.20	1
0.2157	(0.70)	0.7741	0.673	0.759	0.674	13.55	2
0.2053	0.9228	0.8121	0.673	0.7930	0.674	17.70	1
0.22	1.17	0.8383	0.673	0.8133	0.674	21.55	2
0.2194	1.953	0.9363	0.673	0.8872	0.674	31.60	1

TABLE IV. (Curve V., Fig. 1). *Potassium Thiocyanate.*

0.2—0.23	0.2—0.34	0.6900	0.673	0.6868	0.674	1.90	6
0.2673	0.5690	0.7297	0.675	0.7181	0.675	6.40	1
0.2366	1.663	0.7693	0.674	0.7343	0.674	8.90	1
0.2595	2.451	0.8710	0.675	0.8112	0.675	20.10	1

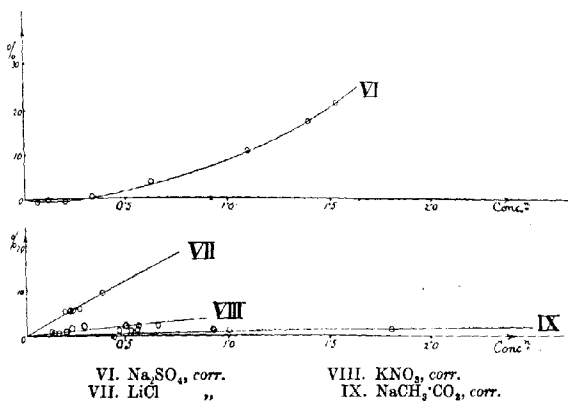
TABLE V. (Curve VI., Fig. 2). *Sodium Sulphate.*

HAc.	Salt.	R_1 .	R_2 .	R_1 (corr.).	R_2 (corr.).	$100 \left[\frac{R_1 - R_2}{R_1} \right]$	Expts.
0.22	(0.07)	0.669	0.673	0.669	0.674	-0.7	5
0.22	(0.13)	0.674	0.673	0.673	0.674	-0.2	8
0.25	(0.22)	0.674	0.675	0.671	0.674	-0.4	7
0.25	(0.35)	0.683	0.675	0.678	0.674	+0.5	5
0.27	(0.61)	0.710	0.677	0.700	0.675	+3.8	2
0.29	1.10	0.762	0.678	0.743	0.675	+10.0	1
0.21	1.40	0.807	0.673	0.786	0.674	+16.6	1
0.22	1.54	0.839	0.673	0.813	0.674	+20.6	1

TABLE VI. (Curve VII., Fig. 2). *Lithium Chloride.*

0.2-0.22	0.2-0.25	0.7143	0.673	0.7116	0.674	5.57	3
0.2249	0.2799	0.7188	0.673	0.7147	0.674	6.00	1
0.2469	0.3930	0.7450	0.674	0.7375	0.674	9.40	1

FIG. 2.



Percentage increase in ratios of acetic acid in distillate and residue due to added salts.

TABLE VII. (Curve VIII., Fig. 2). *Potassium Nitrate.*

0.21	0.22	0.6944	0.673	0.6940	0.674	1.13	2
0.24	0.3-0.5	0.7198	0.674	0.7110	0.674	2.32	2

TABLE VIII. (Curve IX., Fig. 2). *Sodium Acetate.*

0.11	(0.14)	0.6922	0.667	0.6769	0.671	0.8	3
0.1-0.23	0.4-0.67	0.6948	0.671	0.6799	0.673	0.9	7
0.1-0.28	0.9-1.1	0.7001	0.673	0.6799	0.673	1.3	3
0.2900	1.810	0.7244	0.678	0.6834	0.675	1.3	1

The increase of R_1 , the relative concentration of the distillate, for the same solution of acetic acid, that is, the expression

$100\left(\frac{R_1 - R_2}{R_2}\right)$ amounted to no less than 62 per cent. (observed) in the case of 2.3*N*-sodium chloride.

The increase for most salts seems proportional to the concentration of the salt and independent of the concentration of acetic acid.

Curves II—V of Fig. 1 and VI of Fig. 2 show this percentage increase plotted against the concentrations, and they point convincingly towards a straight line function between these two values. Sodium sulphate differs from all the other salts in that the experimental evidence shows a slightly negative effect at lower concentrations, up to about 0.3*N*.

Note on the Calculation of Residues in the Presence of Salts which exhibit a Straight Line Function of the Ratio Increase.

The calculation is similar to the one for the pure acid solution, but we must introduce the functional relation of R_1 with regard to the concentration of the salt.

We have found experimentally for all salts except the sulphate and acetate

$$100\left(\frac{R_1 - R_2}{R_2}\right) = 100K\rho \text{ or } R_1 = R_2(K\rho + 1),$$

in which ρ is the concentration of the salt and K is a constant. Hence $R_1 = R_2\left(\frac{K}{V} + 1\right)$, where V is the volume in litres containing 1 mol. of salt.

If there are y mols. of acetic acid in V litres of the solution in the flask, and a quantity dv of the solution containing dy of the acetic acid distils over, we may set the concentration of the distillate equal to $\frac{dy}{dV} = R_1 \frac{y}{V} = R_2 \left(\frac{K}{V} + 1\right) \frac{y}{V}$. Since $c = \frac{y}{V}$, and by

$$\text{differentiation } \frac{dc}{c} = \frac{dy}{y} - \frac{dV}{V}, \quad \frac{dy}{dV} = c + V \frac{dc}{dV} = R_2 \left(\frac{K}{V} + 1\right)c, \text{ or}$$

$$\frac{dc}{c} = \left(\frac{R_2 K}{V^2} - \frac{R_2 - 1}{V}\right)dV.$$

Integrating,

$$\ln \frac{c_2}{c_1} = R_2 K \left(\frac{V_0 - V_1}{V_0 \cdot V_1}\right) + (R_2 - 1) \ln \frac{V_0}{V_1},$$

or

$$\log \frac{C_1}{C_0} = \frac{1}{2.303} \left[(1 - R_2) \left(\log \frac{V_0}{V_1}\right) + 2.303 + R_2 K \left\{ \frac{V_1 - V_0}{V_1 \cdot V_0} \right\} \right]$$

where C_0 and C_1 are the concentrations and V_0 and V_1 the volumes in the distilling flask before and after distillation.

An alternative formula deducible in the same way is

$$\log \frac{y_0}{y_1} = \frac{R_2}{2.303} \left[2.303 \log \frac{V_0}{V_1} - K \left\{ \frac{V_0 - V_1}{V_0 \cdot V_1} \right\} \right].$$

Either of these expressions can be used to calculate the concentration of the acetic acid in the distilling flask if the initial value of the salt concentration and either its increase or the relative volume of the residual solution are given. They contain two constants. $100K$ is the one which is peculiar to the added salt, and it is simply the percentage increase by 1.0*N*-salt. The other, R_2 , is the ratio of acetic acid in distillate and residue for the same solution in the absence of salt. It is convenient to express V_1 as a fraction of V_0 , the volume at the beginning of the distillation containing 1 mol. of salt; but the initial concentration of salt in mols. per litre = $\frac{1}{V_0}$.

Inspection of the equations show that they are identical with that deduced above for solutions of pure acetic acid, except for the correcting factor $R_2 K \left(\frac{V_0 - V_1}{V_0 \cdot V_1} \right)$. This factor, of course, dis-

appears for large values of V_0 , that is, for very low concentration of added salt. Conversely, for very high concentrations of salt it is predominant, as is evident from the consideration that for, say, 2.6*N*-potassium chloride, no separation takes place, owing to the concentration of acetic acid in the distillate having been so raised as to equal that of the residue. Above such concentrations, the residue becomes weaker instead of stronger.

The general behaviour of a distillation is shown graphically in curve VIA of Fig. 1, which assumes that 1.0*N*-sodium chloride was initially present ($V_0=1$). As the distillation proceeds, the salt accumulates, and the concentration of acetic acid in the residue slowly rises to a maximum where 50 per cent. of the liquid has distilled over ($V_1=0.5$). At this point, $\log \frac{C_1}{C_0} = 0.03$, whence the increase of concentration is 7.2 per cent. At $V_1=0.27$, when 73 per cent. has been distilled over, the concentration of the acid is again the same as it was before the distillation. Beyond this point, the value for $\log \frac{C_1}{C_0}$ assumes rapidly negative values, owing to the high concentration of salt in the residue.

The general equation may be tested by one of our experimental results. Taking the last pair of values in table III for potassium chloride, 1.0*N*-potassium chloride increases the ratio of acetic acid by 18.5 per cent., hence $K=0.185$. Further, $R_2=0.674$,

$V_1 = \frac{1.128}{1.953} V_0$, $V_0 = \frac{1}{1.128}$. These values inserted in the equation lead to the prediction that $C_1 = 1.078C_0$. Experimentally, C_0 was 0.2118*N* (less 1 per cent. for metathesis) and C_1 after distillation 0.2194*N* (plus 5 per cent. for the three corrections). Hence $C_1 = \frac{0.230}{0.210} C_0 = 1.095C_0$. In general, the concentrations observed

appear to agree with the predicted values within about 2 per cent.

To sum up, the process of concentration or separation of the constituents of a binary mixture by means of distillation may thus be considerably accelerated or retarded by the addition of a salt, and will largely depend on the values of the constants R_2 and K , that is, on the nature of the mixture and of the added salt.

(6) Discussion of the Results.

The remarkable effect of a salt on the partial vapour pressure of acetic acid must be evident from the preceding. Comparing the slopes of the various graphs showing the relationship between salt concentration and percentage ratio increase, it appears that the effect is greatest for the chlorides of lithium, sodium, and potassium, and least for sodium acetate. The effect is in all cases independent of the concentration of the acetic acid.

The increase of the concentration of the residue in the flask for acetic acid in aqueous solution during the distillation, not very rapid in itself, is still less if salt is also present. At a concentration of 2.3*N*-sodium chloride, the residue becomes weaker; in other words, the vapour phase in the flask contains more acetic acid than the liquid from which it originates.

For sodium sulphate up to about 0.35*N*, the experimental evidence for the ratio increase seems somewhat complicated. If anything, there is a negative effect, as the course of curve VI in Fig. 2 indicates. Beyond 0.35*N*, the effect is decidedly positive. Between 0.35*N* and 1.1*N*, the graph is practically a straight line, but beyond 1.1*N* its slope appears to increase until, at 1.55*N*, the limit of solubility is approached.

Sodium acetate up to 1.8*N* shows only a very slight effect.

Although the effect of the cation is undeniable (note, for example, the greater slope of the ratio increase for sodium chloride as compared with the one for potassium chloride), the influence of the anion seems to be the predominating factor. The series sodium acetate, potassium nitrate, potassium thiocyanate, sodium sulphate, potassium chloride, lithium chloride, sodium chloride, shows the increase in a progressive degree. It is evident that this order is not that of the Hofmeister or lyotropic series.

It is well known that there is a general qualitative similarity between the effect of neutral salts on such various phenomena as solubilities of gases and non-electrolytes, surface tension, compressibility, maximum density of water, viscosity, dielectric constant, imbibition and gelatinisation of gels, and increase or decrease of rate of catalysis. The explanation of this undoubted parallelism is wholly unknown, and in each individual case there are pronounced exceptions. In the present instance, the exceptions are the acetate and the sulphate, although they may be paralleled by certain cases of catalysis. Possibly in the case of the sulphate our correction for metathesis (formation of HSO_4') has not been sufficiently great. The effects are reconcilable with a solvate form of the dissociation theory.

With regard to the main thesis of this paper, it has now been proved that the reactivity of the undissociated acetic acid is increased by addition of such salts as sodium chloride. A 0.2*N*-solution is affected to the extent of 5.5 per cent. by 0.2*N*-sodium chloride. It was pointed out in the earlier paper (*loc. cit.*) that Walpole's measurements of electromotive force for this particular case gave a result for the hydrogen ion which was 7 or 8 per cent. too high. These two effects, 5.5 and 7 or 8 per cent., are equal within the experimental error, and thus the effect on the dissociation constant deduced for acetic acid cancels out and leaves that constant unchanged by the presence of the salt.

Thus the electromotive force data may be regarded as agreeing with all the other data bearing on this subject, and the experimental evidence all points to the conclusion that the dissociation constants of weak substances are not appreciably affected by the addition of salts. One point we have not investigated, namely, the effect of salts on the chemical potential of the acetate ion.

Summary.

(1) It is shown experimentally that many salts enhance the partial vapour pressure of acetic acid in aqueous solution by very appreciable amounts. In the case of 2.3*N*-sodium chloride, the increase amounts to no less than 62 per cent.

(2) Since this partial pressure is a measure of the reactivity of the undissociated acid in the solution, the undissociated acid must be regarded as exhibiting enhanced chemical potential in the presence of such salts. This is parallel with the available data for the effect of such salts on the measurement of hydrogen ion by electromotive force. The enhancement is thus discovered to be operative on both sides of the chemical equation, and hence to leave the dissociation constant of acetic acid sensibly unaltered.

These experiments remove the only remaining evidence (apart from the ambiguous behaviour of certain insufficiently investigated colloids) for the view that salts might have been regarded as increasing the strength of weak acids.

(3) Whereas a number of salts increase the partial pressure of acetic acid to an extent proportional to the concentration, sodium sulphate exhibits a more complicated behaviour, whilst sodium acetate has only a very slight effect. All electromotive force data on weak acids in the presence of salts other than sodium acetate require to be corrected for the effects here described.

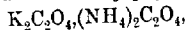
THE CHEMICAL DEPARTMENT,
UNIVERSITY OF BRISTOL.

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CXXV.—Some Ternary Systems containing Alkali Oxalates and Water.

By ALBERT CHERBURY DAVID RIVETT and EDMUND ARTHUR O'CONNOR.

THERE has been considerable discussion at various times regarding the alleged formation of certain double oxalates of the alkali metals. Wenzel is quoted by some early writers as maintaining the existence of the double salts $K_2C_2O_4 \cdot Na_2C_2O_4$ and



but Rammelsberg (*Ann. Phys. Chem.*, 1850, [ii], **79**, 562) has thrown doubt on the one case and Souchay and Lenssen (*Annalen*, 1856, **99**, 31) on the other.

Foote and Andrew (*Amer. Chem. J.*, 1905, **34**, 164) drew the same conclusions as Rammelsberg and Souchay and Lenssen, and claimed to have shown that these double oxalates do not exist at 25° in the solid state. They state that the solid monohydrates of potassium and ammonium oxalates remain in equilibrium with a common saturated solution, and that the same holds for anhydrous sodium and hydrated potassium oxalates. A few years later, Barbier (*Bull. Soc. chim.*, 1908, [iv], **3**, 725) described a double oxalate of potassium and ammonium, stating that it might readily be formed by adding a concentrated solution of potassium oxalate to a saturated solution of ammonium carbonate. The analysis he quotes points to a pure, 1:1, anhydrous double salt.

None of the authors mentioned made complete investigations by the solubility method. Foote and Andrew (*loc. cit.*) obtained a few solubility figures, but to determine the solid phases present they relied on a general principle laid down in a previous paper (*ibid.*, p. 153) that when two salts are mixed in varying proportions and treated with water at a constant temperature, the residue of undissolved solid remains constant in composition and the solution varies if a pure double salt is present, whilst, on the other hand, the residue varies and the solution remains constant in composition when a mere mixture of the two single salts is present. This rule is liable to mislead, if only because it does not take into account the possibility of the formation of mixed crystals (solid solutions).

It has seemed worth while, therefore, to apply the solubility method more fully to some of these ternary systems of alkali oxalates in water. Knowledge of the solid phases present has been obtained by the customary graphic method of plotting in a triangular diagram the percentage compositions of pure solution and of the moist solid (or "residue") in equilibrium with it, and extrapolating the straight line joining the two points to the composition of the pure solid uncontaminated with adhering solution. The systems investigated are those containing potassium, sodium, and ammonium oxalates, in pairs, with water. The solid phases of the individual salts stable at these temperatures with their own aqueous solutions are, respectively, $K_2C_2O_4 \cdot H_2O$, $(NH_4)_2C_2O_4 \cdot H_2O$, and $Na_2C_2O_4$.

EXPERIMENTAL.

I. System: $K_2C_2O_4$ – $(NH_4)_2C_2O_4$ – H_2O at 25° and 50°.

The system potassium oxalate, ammonium oxalate, and water has been examined at 25° and 50°, and the figures obtained are given in tables I and II, respectively, and plotted in Fig. 1.

Suitable mixtures of the salts (monohydrates) and water were heated in bottles, which were sealed and placed in a thermostat, in which they were continuously rotated for about forty-eight hours. Undissolved solid was allowed to settle, and clear solution drawn into a pipette through a small plug of cotton wool held in rubber tubing. A known weight was diluted to a suitable volume for subsequent analyses. Residues were obtained by pouring solution and suspended solid on to a Buchner funnel, drawing the solution through rapidly by means of a pump, but disconnecting the pump before more than a very small amount of air had been

drawn through the moist solid. A slight loss of water vapour at 50° is inevitable, but with rapid working it can be made almost negligible.

Total oxalate was determined by titration of a fraction of the stock solution with standard potassium permanganate, ammonium by distillation with alkali and absorption of ammonia in standard acid, and potassium by difference. Concentrations have been expressed in percentages by weight, but as densities have been determined in all cases, figures for concentrations in other terms are readily obtainable.

TABLE I.

25°.

No.	Density.	Percentage composition of solution or residue (R).			Solid phases.
		$K_2C_2O_4$.	$(NH_4)_2C_2O_4$.	H_2O .	
1	1.021	—	5.01	95.0	$(NH_4)_2C_2O_4 \cdot H_2O$.
2	1.040	2.67	4.72	92.6	Solid solution of $K_2C_2O_4 \cdot H_2O$ in $(NH_4)_2C_2O_4 \cdot H_2O$.
R 2	—	0.44	81.3	18.3	"
3	1.058	4.32	4.48	91.2	"
R 3	—	2.41	56.4	41.2	"
4	1.068	6.51	4.38	89.1	"
R 4	—	2.75	61.1	36.1	"
5	1.087	9.48	4.16	86.4	"
R 5	—	2.62	72.3	25.1	"
6	1.107	12.10	4.01	83.9	"
7	1.124	14.18	3.78	81.0	"
8	1.128	15.37	3.68	80.9	"
9	1.137	16.54	3.57	79.9	"
R 9	—	2.14	80.4	17.2	"
10	1.166	19.39	3.32	77.3	"
R 10	—	4.37	76.4	19.2	"
11	1.185	21.9	3.10	75.0	"
R 11	—	6.70	76.2	19.2	"
12	1.204	24.3	2.90	72.8	"
R 12	—	13.4	61.9	24.7	"
13	1.217	25.9	2.75	71.3	Two solid solutions: (i) $K_2C_2O_4 \cdot H_2O$ in $(NH_4)_2C_2O_4 \cdot H_2O$. (ii) $(NH_4)_2C_2O_4 \cdot H_2O$ in $K_2C_2O_4 \cdot H_2O$.
14	1.216	26.3	1.83	71.9	Solid solution of $(NH_4)_2C_2O_4 \cdot H_2O$ in $K_2C_2O_4 \cdot H_2O$.
15	1.218	26.8	0.85	72.3	"
16	1.215	27.2	—	72.8	$K_2C_2O_4 \cdot H_2O$.

curves are obtainable at each of these temperatures, the two meeting sharply at a quadruple (or condensed triple) point.

There is no evidence at all of the existence of a double salt. On the other hand, it is quite apparent from the relations between compositions of solutions and corresponding residues (shown only for 50°) that the solid phase present in those complexes in which excess of ammonium oxalate is taken (curve *CB*) is not this pure solid, but contains in addition some potassium oxalate. The proportions of the two in the solid vary according to the composition of the solution in equilibrium, and the evidence is definite that mixed crystals of the two salts are produced. The more potassium oxalate there is in the solution, the more there is in the solid. The same must hold with regard to the solids in equilibrium along the curve *AB*. These solids will be mainly potassium oxalate with steadily increasing proportions of ammonium oxalate. The amounts of ammonium oxalate in solutions along this curve are, however, so small that a slight error in the analysis of the residue may make the extrapolation method uncertain in showing the solid phase.

Some of the mixed crystals were dried by draining on a porous tile in a closed vessel immersed in the thermostat. Analysis proved the two constituents of these mixed crystals to be the respective monohydrates.

The form of the isotherms, with a sharp change of direction at *B*, shows that two distinct solid phases must be present at this, a univariant, point. It follows that the series of mixed crystals is not complete, but that there is a limit to the solubility of each solid in the other. These limits have not been determined. The compositions are also not given by such points as *D* and *E* in Fig. 1, those of the exact solid solutions in equilibrium with the corresponding liquid solutions at the other ends of the tie-lines. Some of the crystals may have had a core of the pure main constituent, so that the mean composition represented by *D* and *E* may be low in potassium oxalate as compared with the solid solution itself. All that is established is the existence of mixed crystals.

The work of Foote and Andrew (*loc. cit.*) is not quite extended enough to show this. They obtained only the points *A*, *B*, and *C* at 25°.

It has been found impossible to repeat the work of Barbier (*loc. cit.*), which pointed to the formation of an anhydrous double salt, $K_2C_2O_4 \cdot (NH_4)_2C_2O_4$. By following closely the method which he described for isolating the compound, crystals were precipitated which, after drying on a porous tile, contained 81.1 per cent. of

SYSTEMS CONTAINING ALKALI OXALATES AND WATER. 1351

ammonium oxalate, 5.8 per cent. of potassium oxalate, and (by difference) 13.1 per cent. of water. After washing with a solution of ammonia, as recommended by Barbier, the proportion of potassium oxalate decreased slightly. It appears certain that this precipitate consists of mixed crystals of the two hydrates.

It is of interest to note that Souchay and Lenssen (*loc. cit.*), following Wenzel's instructions for preparing the alleged double salt, obtained crystals which they stated to be ammonium oxalate, but containing 0.9 per cent. potash.

II. System: $\text{Na}_2\text{C}_2\text{O}_4-(\text{NH}_4)_2\text{C}_2\text{O}_4-\text{H}_2\text{O}$ at 25° and 50° .

Sodium oxalate differs from both the potassium and ammonium salts in crystallising anhydrous from aqueous solution; hence it is less likely that mixed crystals will be formed between it and either of the other two. The figures in tables III and IV show that neither double salt nor mixed crystals occur in the sodium-ammonium system at 25° or 50° . The method of analysis was similar to that adopted for the previous system.

TABLE III.

25° .

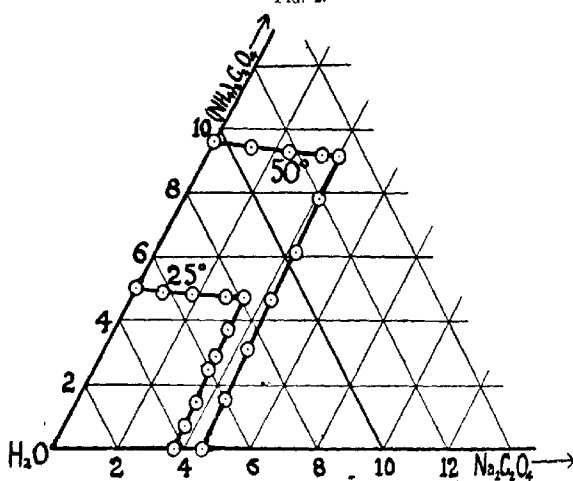
No.	Density.	Percentage composition of solution or residue (R).			Solid phases.
		$\text{Na}_2\text{C}_2\text{O}_4$.	$(\text{NH}_4)_2\text{C}_2\text{O}_4$.	H_2O .	
1	1.027	3.73	—	96.3	$\text{Na}_2\text{C}_2\text{O}_4$.
2	1.030	3.69	0.74	95.6	"
3	1.033	3.65	1.49	94.6	"
R 3	—	63.9	0.53	35.6	"
4	1.037	3.50	2.48	94.0	"
5	1.039	3.51	2.89	93.6	"
6	1.043	3.46	3.77	92.8	"
* 7	1.047	3.41	4.74	91.8	$\text{Na}_2\text{C}_2\text{O}_4$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.
8	1.043	2.85	4.75	92.4	$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.
9	1.035	1.82	4.81	93.4	"
R 9	—	0.40	66.9	32.7	"
10	1.028	0.89	4.88	94.2	"
11	1.021	—	5.01	95.0	"

TABLE IV.

50°.

No.	Density.	Percentage composition of solution or residue (R).		H ₂ O.	Solid phases.
		Na ₂ C ₂ O ₄ .	(NH ₄) ₂ C ₂ O ₄ .		
1	1.023	4.54	—	95.5	Na ₂ C ₂ O ₄ .
2	1.031	4.46	1.59	94.0	"
3	1.036	4.37	3.14	92.5	"
4	1.044	4.28	4.64	91.1	"
R 4	—	70.0	1.47	28.5	"
5	1.049	4.29	6.12	89.6	"
6	1.056	4.13	7.86	88.0	"
R 6	—	56.7	3.54	39.8	"
7	1.063	4.05	9.19	86.8	Na ₂ C ₂ O ₄ and (NH ₄) ₂ C ₂ O ₄ ·H ₂ O.
8	1.059	3.57	9.21	87.2	(NH ₄) ₂ C ₂ O ₄ ·H ₂ O.
R 8	—	1.47	63.4	35.1	"
9	1.051	2.45	9.32	88.2	"
10	1.042	1.25	9.46	89.3	"
11	1.034	—	9.63	90.4	"

FIG. 2.



The results are plotted in Fig. 2, where, on account of the sparing solubilities of the two components, only a single angle of the triangle is shown. The residues are omitted.

III. System: K₂C₂O₄-Na₂C₂O₄-H₂O at 25°.

Footé and Andrew (*loc. cit.*) concluded that anhydrous sodium oxalate and the monohydrate of potassium oxalate can exist side

by side in equilibrium with a common saturated solution, and the figures in table V, plotted in Fig. 3, confirm this, showing that neither double salts nor mixed crystals are formed. Solutions and residues were analysed by determining total oxalate by titration and total anhydrous salts by weighing after evaporation and drying at 125°, at which temperature potassium oxalate monohydrate is readily dehydrated. As the amount of sodium oxalate present is always relatively small, this indirect method is less accurate than that employed in the previous two cases.

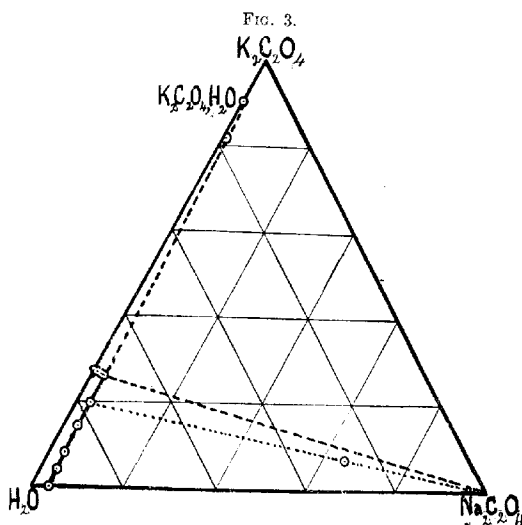


TABLE V.
25°.

Percentage composition of solution
or residue (R).

No.	Density.	$K_2C_2O_4$.	$Na_2C_2O_4$.	H_2O .	Solid phases.
1	1.215	27.2	—	72.8	$K_2C_2O_4 \cdot H_2O$.
2	1.218	26.8	0.77	72.4	"
3	1.223	26.3	1.71	72.0	"
4	1.226	26.2	2.17	71.6	"
R 4	—	81.9	0.73	17.4	"
5	1.228	26.1	2.50	71.4	$K_2C_2O_4 \cdot H_2O$ and $Na_2C_2O_4$.
6	1.178	19.8	3.21	77.2	$Na_2C_2O_4$.
R 6	—	7.00	65.3	27.7	$Na_2C_2O_4$.
7	1.135	14.4	3.21	82.4	"
8	1.084	8.10	3.40	88.5	"
9	1.057	3.99	3.71	92.3	"
10	1.026	—	3.71	96.3	"

Summary.

(1) It has been stated by some authors and denied by others that potassium and ammonium oxalates form a double salt. Isotherms have been obtained at 25° and 50°, and show that at these temperatures mixed crystals of the monohydrates are formed.

(2) Anhydrous sodium oxalate has been shown to exist in equilibrium with ammonium oxalate monohydrate and a common, saturated solution at 25° and 50°. Neither double salts nor mixed crystals are formed.

(3) The same has been shown to be the case at 25° with anhydrous sodium oxalate and potassium oxalate monohydrate.

UNIVERSITY OF MELBOURNE.

[Received, November 1st, 1919.]

CXXXVI.—*The Decomposition of Carbamide in the Presence of Nitric Acid.*

By TUDOR WILLIAMS PRICE.

WHILE investigating the use of dilute nitric acid as a nitrating agent at elevated temperatures, it was found that nitration was entirely inhibited by the addition of carbamide, although all the acid was used up. This reaction was considered worthy of further investigation, the results of which are given in the present communication.

The action of concentrated nitric acid on carbamide nitrate in the solid state at the ordinary temperature has been studied by Franchimont (*Rec. trav. chim.*, 1884, **3**, 216), who found that a gas was given off slowly, consisting of equal parts of carbon dioxide and nitrous oxide. The volume of gas was such that it contained all the carbon of the carbamide as carbon dioxide, and half the nitrogen as nitrous oxide, the other half forming ammonium nitrate.

No account has been found in the literature of the action of dilute nitric acid on carbamide, although the action of hydrochloric acid and sulphuric acid has been studied by Fawsitt (*Zeitsch. physikal. Chem.*, 1902, **41**, 601) and of hydrochloric acid by Werner (*T.*, 1918, **113**, 84).

Fawsitt (*loc. cit.*) found the reaction between carbamide and dilute hydrochloric and sulphuric acids to be unimolecular, which

he explained by the assumption that the former is first transformed to a small extent into ammonium cyanate at a measurable rate, and, if the inverse change is neglected, according to a unimolecular reaction. The ammonium cyanate is thereupon decomposed into the ammonium salt of the acid used, and carbon dioxide at a much greater rate than that at which ammonium cyanate is formed, and thus the decomposition of carbamide in the presence of hot acids is almost identical with the rate at which it is transformed into ammonium cyanate.

Werner (*loc. cit.*), on the other hand, states that the above assumption is quite unnecessary, and that the velocity of the reaction is regulated by the rate of dissociation of carbamide (at 100°) into ammonia and cyanic acid, when both products of dissociation are removed practically as fast as they are generated.

Whichever scheme of the mechanism of the reaction is correct, the final products are the same, namely, carbon dioxide and the ammonium salt of the acid used. If the action of hot dilute nitric acid on carbamide is the same as that of hydrochloric acid, the reaction should be unimolecular, and the products should be carbon dioxide and ammonium nitrate.

Veley (*Proc. Roy. Soc.*, 1892, 52, 27) has shown that nitric acid decomposes slowly at high temperatures, forming nitrous acid, the weaker the acid the higher being the temperature required for decomposition; also, it is well known that carbamide decomposes nitrous acid very readily, forming carbon dioxide and nitrogen. Hence it is possible that the true explanation of the disappearance of nitric acid when heated with carbamide in solution is the alternate formation of nitrous acid from nitric acid, and decomposition of the nitrous acid by carbamide. In this case, nitrogen will be present in the evolved gas, as well as carbon dioxide.

There are thus three separate methods of decomposition of carbamide by nitric acid, the gaseous products in each case being different. An analysis of the gas produced will then be of extreme importance.

As will be seen in the experimental part, the reaction between carbamide and nitric acid is unimolecular, and the gas evolved consists entirely of carbon dioxide.

EXPERIMENTAL.

The carbamide used was ordinary commercially pure carbamide recrystallised four times from absolute alcohol. The nitric acid solutions were made from pure distilled nitric acid, and contained

only a trace of nitrous acid. A normal solution of carbamide is taken to be one containing half its molecular weight in grams in a litre of water; all the other solutions of carbamide were made up on this basis.

Ten c.c. of the mixed solutions of carbamide and nitric acid were placed in hard-glass test-tubes, which were then sealed and placed in water at the required temperature. After various periods of heating, the tubes were withdrawn, cooled, opened, and their contents titrated with standard sodium hydroxide solution, using methyl-orange as indicator.

The majority of the experiments were made at 100°, but the reaction between *N*/2-carbamide and *N*/2-nitric acid was studied at 70°, 80°, 90°, and 100°.

The influence of certain salts on the velocity of the reaction was also examined.

In order to obtain figures comparable with those of Fawsitt, the velocity-constants for a unimolecular reaction were calculated according to the equation

$$k = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2},$$

instead of the correct equation,

$$k = \frac{1}{t_2 - t_1} \log_e \frac{a - x_1}{a - x_2},$$

where *a* is the initial concentration of carbamide, *x*₁ the amount of carbamide decomposed in time *t*₁, and *x*₂ the amount decomposed in time *t*₂. In every case, *t*₁ was fixed at sixty minutes, so as to obviate the error due to the time taken for the tube to reach the desired temperature.

a, *x*₁, and *x*₂ were obtained from the titre of sodium hydroxide immediately after mixing the two solutions, and the titre after times *t*₁ and *t*₂.

In one case, the constants for a bimolecular and termolecular reaction were calculated.

Results.—The results of two experiments are given in detail, and all are summarised in table I. It will be noted that the velocity-constant tends to increase towards the end of an experiment, and this is much more marked with *N*- and 2*N*-solution than with the more dilute ones.

Experiment 3. *N*-Carbamide + *N*-Nitric Acid at 100°. $a = 50.40$.

Time in minutes.	$a - x$.	$k_1 \times 10^5$ (unimolecular).	$k_2 \times 10^5$ (bimolecular).	$k_3 \times 10^7$ (termolecular).
60	45.50	—	—	—
120	40.51	84	45	84
180	35.68	84	50	101
270	29.53	89	58	127
360	24.21	91	64	163
480	17.84	(97)	—	—
600	13.35	(98)	—	—
960	5.18	(105)	—	—
1500	1.21	(109)	—	—

 Mean value $k \times 10^5 = 87$.

 Experiment 5. *N*/2-Carbamide + *N*/2-Nitric Acid at 100°. $a = 25.43$.

Time in minutes.	$a - x$.	$k \times 10^5$.
60	22.75	—
120	19.61	101
180	17.25	100
270	13.96	101
360	11.39	100
480	8.29	105
600	6.36	102
900	3.00	104
1200	1.42	107
1500	0.83	(169)

 Mean value $k \times 10^5 = 102$.

TABLE I.

Showing Velocity-constants obtained in the Decomposition of Carbamide.

Concentration of reaction mixture.	Tem- perature.	Dura- tion of expt. in minutes.	No. of observa- tions.	Mean value of $k \times 10^5$.	Maxi- mum varia- tion of k from mean.
2 <i>N</i> -Carbamide + 2 <i>N</i> -HNO ₃ ...	100°	420	7	73	2.0
2 <i>N</i> . " + <i>N</i> -HNO ₃ ...	100	270	6	105	4.0
<i>N</i> . " + <i>N</i> -HNO ₃ ...	100	360	5	87	4.0
<i>N</i> /2. " + <i>N</i> -HNO ₃ ...	100	1800	9	88	3.0
<i>N</i> /2. " + <i>N</i> /2-HNO ₃ ...	100	1200	9	102	5.0
<i>N</i> /4. " + <i>N</i> /2-HNO ₃ ...	100	600	5	108	2.0
<i>N</i> /4. " + <i>N</i> /4-HNO ₃ ...	100	420	7	111	3.0
<i>N</i> /8. " + <i>N</i> /8-HNO ₃ ...	100	420	6	116	6.0
<i>N</i> /16. " + <i>N</i> /16-HNO ₃ ...	100	360	7	133	8.0
<i>N</i> /2. " + <i>N</i> /2-HNO ₃ ...	100	1500	10	122	5.0
" + <i>N</i> /2-NH ₄ NO ₃ ...					
<i>N</i> /2. " + <i>N</i> /2-HNO ₃ ...	100	900	9	118	6.0
" + <i>N</i> /2-KNO ₃ ...					
<i>N</i> /2. " + <i>N</i> /2-HNO ₃ ...	100	420	5	118	3.0
" + <i>N</i> /2-NH ₄ Cl ...					
<i>N</i> /2. " + <i>N</i> /2-HNO ₃ ...	100	600	8	116	3.0
" + <i>N</i> /2-KCl ...					
<i>N</i> /2. " + <i>N</i> /2-HNO ₃ ...	89	1800	9	23.0	2.8
<i>N</i> /2. " + <i>N</i> /2-HNO ₃ ...	80	2790	9	9.3	0.7
<i>N</i> /2. " + <i>N</i> /2-HNO ₃ ...	70	9360	10	2.4	0.3

Experiment 17.—Twenty-five c.c. of *N*-carbamide and 25 c.c. of *N*-nitric acid were heated at 100° in a boiling tube fitted with a reflux condenser. A delivery tube connected the top of the condenser to a nitrometer. The total air space from the level of the liquid in the boiling tube to the nitrometer was 34 c.c. One hundred c.c. of gas were collected in the nitrometer and rejected. It was considered that by this time all the air had been swept out of the apparatus, and collection of the gas for analysis was commenced. Fifty c.c. of this gas were almost entirely absorbed by a piece of moist potassium hydroxide, only a minute bubble being left. The gas was thus composed entirely of carbon dioxide, and did not contain any nitrous oxide or nitrogen, the small residue being either air which had not been completely swept out of the apparatus, or nitrogen from the trace of nitrous acid present in the nitric acid.

The heating of the carbamide and nitric acid solution was continued for fifty hours, at the end of which the solution was evaporated to dryness. On analysis, the residue was found to consist of ammonium nitrate with a little unchanged carbamide.

Discussion of Results.

The results show that the reaction between carbamide and nitric acid in dilute solution is undoubtedly unimolecular. The products consist entirely of carbon dioxide and ammonium nitrate. Hence the reaction is analogous to the decomposition of carbamide by hydrochloric or sulphuric acid, and is not due to the preliminary decomposition of nitric acid into nitrous acid with subsequent decomposition of the latter by carbamide.

On comparing the results with those obtained by Fawsitt for hydrochloric acid in table II, it will be seen that at all dilutions the velocity of reaction is greater with nitric acid than with hydrochloric acid.

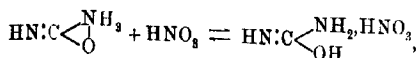
TABLE II.

Showing Comparison between Velocity of Reaction at 100° of Carbamide with Nitric Acid and Hydrochloric Acid.

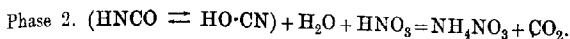
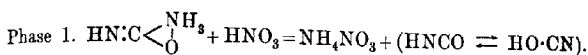
				$k \times 10^4$	
Reaction mixture.				HNO ₃ .	HCl.*
2 <i>N</i> -Carbamide	+ 2 <i>N</i> -acid	73	—	
<i>N</i> .	+ <i>N</i>	87	58	
<i>N</i> /2.	+ <i>N</i> /2.	107	77	
<i>N</i> /4.	+ <i>N</i> /4.	111	90	
<i>N</i> /8.	+ <i>N</i> /8.	116	101	
<i>N</i> /16.	+ <i>N</i> /16.	133	101	

* Fawsitt's results.

The velocity of reaction diminishes regularly with an increase in the concentration of the nitric acid, and no maximum point was found such as Fawsitt found for hydrochloric acid (*loc. cit.*, p. 612). Fawsitt and Werner both state that only free carbamide is active. According to Werner, the equilibrium between carbamide and its nitrate can be represented as follows:



and the reaction between carbamide and nitric acid, on the analogy of the reaction between carbamide and hydrochloric acid, can be represented thus:



The diminution of the velocity with increase in concentration of the acid can thus be explained, since it is only "free" carbamide, and not carbamide "fixed" as its nitrate, which takes part in Phase 1 of the reaction.

Fawsitt found that the decomposition of carbamide in the presence of hydrochloric acid was retarded slightly by the addition of ammonium chloride, but was accelerated in the presence of sulphuric acid by the addition of ammonium sulphate. He also found that the decomposition of carbamide in the presence of water alone was accelerated by the addition of ammonium carbonate, sodium chloride, and potassium chloride, whilst ammonium chloride and ammonium hydrochloride had a decided retarding effect.

In the presence of nitric acid, the present author has found that ammonium nitrate, potassium nitrate, ammonium chloride, and potassium chloride all have a distinct accelerating effect on the decomposition of carbamide at *N/2*-concentration.

According to the dissociation theory of the decomposition of carbamide, the first action of heat on it is the production of ammonia and cyanic acid; in the presence of acids, this is followed by combination of ammonia with acid, forming an ammonium salt, and by hydrolysis of cyanic acid, forming an ammonium salt and carbon dioxide. The addition of the ammonium salt, or of any salt containing an ion common with the ammonium salt, to the reaction mixture, should therefore have a retarding effect on the velocity of decomposition. As shown by the experiments, this is not the case when carbamide is decomposed in the presence of nitric acid, and hence it would seem that the dissociation theory of

the decomposition of carbamide is not applicable in the presence of nitric acid.

The great influence of temperature on the velocity will be seen from table III.

TABLE III.

Showing Effect of Temperature on Velocity of Reaction between N/2-Carbamide and N/2-Nitric Acid.

Temperature.	$k \times 10^4$.
100°	102.0
89	23.0
80	9.3
70	2.4

Below 80°, the velocity of decomposition of carbamide is small, and at 30° to 40° would be negligible; hence the use of excess of carbamide for the removal of nitrous acid from a mixture of nitrous acid and nitric acid will not be accompanied by loss of nitric acid as such if the temperature is not allowed to rise above 40°.

In conclusion, the author's best thanks are due to Messrs. Nobel's Explosives Company, Limited, and to Mr. William Rintoul, Manager of the Research Section, for the facilities afforded for carrying out this work and for permission to publish the results.

THE RESEARCH LABORATORIES,
ARDEER.

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CXXXVII.—*Studies in Catalysis. Part XII. Catalytic Criteria and the Radiation Hypothesis.*

By WILLIAM CUDMORE MCCALLAGH LEWIS.

THE criteria which have been suggested from time to time as applying to the phenomenon of catalysis are as follows (compare Rideal and Taylor, "Catalysis in Theory and Practice," Chap. 2):

- (1) The chemical composition of the catalytic agents is unchanged on completion of the reaction process.
- (2) Minimal amounts of a catalytic agent are adequate for the transformation of large quantities of the reacting substances.
- (3) A catalyst does not affect the final state of equilibrium.
- (4) A catalyst modifies the velocity of two inverse reactions to the same degree.

(5) A catalytic agent is incapable of starting a reaction; it can only modify the velocity of the reaction.

Criteria (1) and (2) are closely related, (2), in fact, being the corollary of (1). Both would be accepted at once provided secondary effects are excluded. To this extent they state a fact of experience, and indicate that catalysis is simply a special case of ordinary chemical reactivity.

Criteria (3) to (5), which form a group by themselves, are in a different category, as representing generalisations which may or may not be true. Criterion (4) is the corollary of (3), so that the group contains two distinct criteria. Considerable difference of opinion exists at the present time regarding the validity of these conclusions, according to the point of view adopted as the basis of criticism. It is of some interest, therefore, to examine criterion (3) or (4) and criterion (5) from the point of view of the radiation hypothesis of chemical reactivity.

We shall consider criterion (5) in the first place. On the radiation hypothesis, the possibility of a reaction occurring depends on the existence of radiation of a type or frequency absorbable by the reacting substance, the quantum of which radiation is sufficiently large to communicate the necessary critical increment to the molecule. In the case of thermal radiation, which is the kind of radiation envisaged in the quantum theory, theoretically all possible wave-lengths or frequencies are represented at any temperature. Consequently, the type of radiation necessary for any reaction is present in the space occupied by the matter, and therefore every reaction is correspondingly possible. This must include the so-called catalytic reactions as well as those to which his name is not applied. From this point of view, therefore, can we conclude that a catalyst does not initiate, but simply accelerates, a process which would occur, although under certain conditions infinitely slowly? This cannot be affirmed without qualification.

In the form in which criterion (5) is stated, it is evidently assumed that the same process *may* occur whether the catalyst be present or not, but this assumption is not necessarily true. It seems necessary to ascribe in certain cases, if not in all, a definite stoichiometric molecular mechanism to a catalyst, just as one would to any other reactant, and consequently, by adding such a catalyst, a new process commences (the origin of which is the field of radiation) that happens to give rise to certain end-products, which, we believe, might be attained in the absence of the catalyst. The fact appears to be that criterion (5), as ordinarily stated, involves a false antithesis. From the point of view of the radia-

tion hypothesis, a catalyst may be said either to render a reaction possible by supplying the necessary matter, or it may merely accelerate, according to circumstances. In no case is it the fundamental initiator of a process. The rôle played by the catalyst may be conveniently illustrated by the catalytic effect of an acid in the inversion of sucrose or the hydrolysis of an ester. Prior to the addition of the acid, the reaction is possible, involving reaction between a molecule of sucrose or ester and either a molecule of water or its ions, probably the undissociated molecule. On addition of the catalysing acid, the hydrogen ion accelerates the process already begun by the hydrogen ions already present. The undissociated molecule of the acid may also accelerate the reaction, but in doing so it is almost certain that it produces an intermediate substance, which was not formed in its absence. In so far as the intermediate stage is concerned, the molecule of the acid has rendered a new intermediate process possible, although the final products are independent of the nature of this intermediate stage. The real source or origin of initiation of any reaction, on the radiation hypothesis, is the radiation itself. The material catalyst, if it acts simply as a transformer, hastens a reaction which radiation has already initiated. The catalyst may also act as a molecular reactant, giving rise, under the stimulus of radiation, to new intermediate products. The validity of conclusion (5) depends, therefore, on the particular view adopted regarding the mechanism of the process. It seems that two distinct modes of mechanism are possible, and are apparently realised in the well-known acid catalyses. On one mode, the catalyst simply accelerates; on the other, it renders a new mechanism possible from the material point of view.

Turning now to criterion (3) or (4), which possesses much greater practical significance, the radiation hypothesis leads to the conclusion that, as a general principle, criterion (3) or (4) is certainly not true.

Let us take the simplest possible case of reversible reaction, represented by



The substance A is characterised by being capable of absorbing radiation of frequency ν_A , as a result of which it is transformed into B . The substance B is likewise capable of absorbing radiation of frequency ν_B , as a result of which the process is reversed. The heat evolved, Q , on passing from A to B , is then given by the expression -

$$Q = Nh(\nu_B - \nu_A),$$

where N is the Avogadro number and Q is referred to one gram-molecule of A transformed.

Let us consider the special case in which $v_A = v_B$, or approximately so. In this case, Q is zero, or approximately so. A catalyst acting as a transformer will in this case be unable to distinguish between the two types of molecules A and B , since each is capable of absorbing the same type, or approximately the same type of radiation. It will therefore catalyse both the direct and the reverse reaction equally. That is, the opposing velocity constants will be equally increased, and the equilibrium constant will remain unaffected by the presence of the catalyst. This result is in harmony with the criterion.

If, on the other hand, the heat of the process is considerable, that is, v_A differs considerably from v_B , then it no longer follows that a positive catalyst will equally accelerate both reactions. In general, it would not be expected to do so, and consequently, in general, the equilibrium point will be affected by the catalyst. It is a significant fact, in view of the conclusion just drawn, that those reactions, such as esterification or hydrolysis, in which the equilibrium point is not sensibly affected by the catalyst, are precisely those in which the heat effect is small.

In the above case we have been considering mainly homogeneous catalysis by means of ions. Let us now take the case of catalysis by the undissociated molecule, such as the molecule of hydrochloric acid, which is generally regarded as functioning through the formation of an intermediate ternary compound. Thus, Falk and Nelson (*J. Amer. Chem. Soc.*, 1915, **37**, 1732) represent the intermediate oxonium complex in the case of hydrolysis of esters as (ester, $\text{HCl} \cdot \text{H}_2\text{O}$). In the reverse process, the corresponding compound is (carboxylic acid, $\text{HCl} \cdot \text{alcohol}$). These two compounds are tautomeric, and may be identical. If they are identical, as Falk and Nelson assume, then the hydrochloric acid molecule will equally affect the direct and the reverse process, and thus leave the equilibrium point unchanged. This explanation of the mechanism of the effect produced by the undissociated molecule of the catalysing acid has certainly the advantage of simplicity. It has this implication, however. Such additive compounds are generally formed rapidly compared with the rate of any further decomposition which they may undergo. If this is so, and if the same intermediate compound is formed in the hydrolysis as in the esterification, it would follow that the velocity constants should be the same, and the equilibrium constant should therefore be unity. This is not in agreement with experiment, although it is significant that the value of K is not greatly removed from unity. Thus, experiment has shown that

$$K = \frac{[\text{methyl acetate}] \times [\text{water}]}{[\text{methyl alcohol}] \times [\text{acetic acid}]} = 4.6$$

(compare Part V of this series of papers, T., 1916, 109, 71).

This ratio means that the velocity constant of esterification is 4.6 times the velocity constant of hydrolysis. On the radiation view, this ratio is mainly determined by the relative value of the exponential terms, that is, by

$$e^{-Nh\nu_1/RT} / e^{-Nh\nu_2/RT},$$

where $Nh\nu_1$ is the critical increment of esterification and $Nh\nu_2$ is the critical increment of hydrolysis, that is,

$$e^{Nh(\nu_2 - \nu_1)/RT} = 4.6.$$

At 300° absolute we find, therefore, that $\nu_2 - \nu_1 = 1 \times 10^{13}$. Both ν_1 and ν_2 do not, however, lie very far from the value 2×10^{14} , so that the difference in respect of position of absorption of infra-red radiation is extremely small, being of the order of one-twentieth of the absolute value of either frequency. The same idea is conveyed by saying that the heat effect does not exceed 1000 calories. The fact, therefore, that the equilibrium constant possesses a value not unity, but not far removed therefrom, means on the radiation basis that the intermediate compounds are not identical, but tautomeric, and, further, that both kinds of molecule absorb almost the same frequency, so that any change in the equilibrium constant introduced by altering the concentration of the catalyst is insensible. (It may be noted that the relatively large change in K observed by Lapworth has its origin, as Lapworth has shown, in what is virtually a distinct reaction not directly connected with the actual esterification-hydrolysis process itself.) In the case considered we conclude, therefore, that as a practical guide the criterion (3) or (4) is true, that is, in those cases in which the equilibrium constant is not far removed from unity. The conclusion is obviously comparable with that drawn in connexion with ion catalysis.

In addition to homogeneous catalysis by dissolved substances in a given solvent, it is well known that different solvents themselves exert their own catalytic effect. From the point of view of radiation, we conclude that in this type of catalysis criterion (3) or (4) cannot, in general, be even approximately true, since each solvent is characterised by its own electromagnetic properties, that is, by its power of absorption at different wave-lengths, which differs from solvent to solvent, and consequently entails a different distribution of radiation density. The particular type of radiation required by the reactant is therefore present to a different extent according to the nature of the solvent, and consequently the

velocity constant and equilibrium constant is a function of the solvent. Specific differences are further introduced by the mutual interaction of solvent and solute, whereby the effective frequency itself is altered to a slight extent.

Finally, as regards heterogeneous catalysis, evidence has been collected and presented by Bancroft (*J. Physical Chem.*, 1917, **21**, 573; 1918, **22**, 433) to show that the catalyst affects the equilibrium point of the process. Heterogeneous catalysis has been examined in a preliminary manner from the point of view of radiation (T., 1919, **115**, 182), and it is concluded that the equilibrium point must be a function of the nature and extent of the catalytic material, owing to the alteration in the values of the critical increments which is introduced by the presence of the catalyst. The catalytic layer here considered is only one molecule, or possibly two molecules, in thickness, that is, it is of the order 10^{-8} cm. In this layer, the final amounts of reactants and resultants will differ, in general, from the true equilibrium amounts characteristic of the homogeneous gas phase, for in the adsorption layer the relative amounts are determined by the relative adsorption capacities. If this is a complete statement of the phenomenon, it is evident that criterion (3) or (4) is inapplicable. There is, however, a further possibility to be considered.

The adsorbed reactants and resultants are in an activated condition as long as they are actually in the adsorption layer. In time, they necessarily pass out into the homogeneous gas phase, owing to desorption. If these molecules at the moment of leaving the adsorption layer lose the extra energy which they possess and become immediately transformed into molecules of normal energy content, it follows that their relative concentration in the homogeneous gas phase becomes identical with that in the adsorption layer, for, in general, the reaction in the homogeneous phase is extremely slow. There is the possibility, however, that the activated reactants and resultants on leaving the true adsorption layer do not immediately revert to the inactive state, but may retain their activity for a short space corresponding, perhaps, with a layer 10^{-6} cm. in thickness. If this is the case, there will be a rapid chemical change in this extra-adsorption layer, which will tend to bring the concentrations of the reactants and resultants into the ratio required by the law of mass action for the homogeneous phase. Whether the true equilibrium point would be attained or not would depend on the average life of the activated molecules. At moderately high temperatures, the average molecular velocity may be taken to be 10^5 cm. per second; hence it would require 10^{-11} second for a molecule to traverse a distance

of 10^{-6} cm. It is possible that the activated state may be maintained for a longer period of time than this, and therefore the more likely is the process to attain the true equilibrium position. The more selective the nature of the adsorption material, the further, in general, will the "equilibrium" of the adsorption layer depart from the true mass action equilibrium. Hence, even if such a compensating effect as that suggested above actually operates, criterion (3) or (4) cannot be regarded as valid.

It is concluded, therefore, that criterion (3) or (4) is, in general, not true; in homogeneous systems it approximates more closely to experiment the smaller the heat effect accompanying the reaction; in heterogeneous systems it is not certain whether even this approximation to validity holds good.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

[Received, October 31st, 1918.]

CXXVIII.—*Criteria of the Degree of Purity of Commercial Toluene.*

By JOHN SCOTT LUMSDEN.

THE following investigation was undertaken for the Explosives Department of the Ministry of Munitions for the purpose of finding some easily applied method for estimating the degree of purity of commercial toluene, and is published with the permission of the Department.

Commercial toluene contains varying amounts of a liquid which cannot be nitrated and has distilled along with the toluene during rectification. This liquid has not been isolated, but in the following tests the assumption is made that it may be represented by a paraffin mixture which boils close to the boiling point of toluene. By fractionation of petrol, a quantity of such a liquid was obtained boiling at $108-112^{\circ}$.

Estimation of Toluene by Specific Gravity.—Pure toluene at 15° was found to have D 0.8712; the paraffin mixture had D 0.743. Since there is no change in volume on mixing toluene and paraffin, a graph was prepared to show the density of mixtures. From this graph, it was found that the presence of 1 per cent. of paraffin produced a lowering of the density of 0.0013.

Whilst such a graph may not be depended on to give the accurate

percentage of impurity present, because the toluene may be moist and the impurity may not be like that assumed, it is certainly useful in indicating poor samples. For example, of two samples of commercial toluene, (a) had D 0.872 and (b) 0.8613. Both were fractionated, with the following results: Sample (a) showed a trace of moisture, then boiled steadily at 110°. All fractions, right to the end, had D 0.8716. This was therefore a very good sample of toluene. Sample (b) showed a little moisture, and then boiled half a degree below, slowly rising to half a degree above 110°. The fractions had D 0.8623, 0.8621, 0.8622, 0.8619, 0.8612, 0.8586, and 0.8570. The original low density and the decreasing density of the fractions pointed to a considerable admixture of paraffins; from the graph, the indication is 7.7 per cent.

Estimation of Toluene by Nitration.—To effect nitration, potassium nitrate and sulphuric acid were employed, as described later. It was soon found that the nitration of toluene cannot be made to stop when the mononitro-compound is formed, but that any excess of acid is used up, producing the dinitro-compound; it was, however, proved, as the result of many experiments, that nitration stops quantitatively when all the toluene has been converted into the dinitro-compound.

Using nitration as a means of estimating toluene, there are obviously two methods which may be adopted, namely, by nitrating with a weighed excess of potassium nitrate, and determining the weight of nitric acid remaining after nitration, the amount of acid used is obtained, and from that the weight of toluene nitrated, or by isolating and weighing the dinitro-compound. Adopting the first method, it was found that the residual acid could be satisfactorily determined by the nitrometer, but that by the second method the dinitro-compound could not be completely recovered, because a small but definite amount remains in solution in the acid liquid from which the substance is filtered.

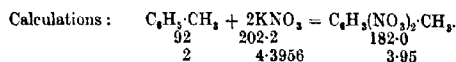
The nitration process is as follows. A 100 c.c. flask is weighed, and into this is weighed accurately, by dropping from a fine pipette, 2 grams of the sample to be nitrated. Five grams of pure dry powdered potassium nitrate are weighed in a watch-glass or aluminium scoop, and transferred with great care to the flask. The flask is cooled in water, and 30 c.c. of pure concentrated sulphuric acid are poured in rapidly, the flask being shaken continuously to prevent the formation of solid lumps, which, if formed, take some time to dissolve. When the action is over, a pale yellow, homogeneous liquid is obtained.

To cause the dinitro-compound to separate, about 60 c.c. of water are added, the first few c.c. being dropped in slowly, lest

the heat evolved should volatilise any nitric acid, and at the same time the flask is cooled in water.

The solid is obtained in soft flakes which are nearly white, and when the contents of the flask are quite cold, the separation may be considered complete. Filtration is effected by the aid of the pump, using a small porcelain funnel with a small filter paper; the preparation flask is washed out with several small amounts of water, which are poured through the funnel, and the solid is washed free of acid. The filtrate is transferred to a graduated cylinder, and, together with the washings of the filter flask, is made up to exactly 150 c.c.

The whole operation of nitration proceeds smoothly, and the only point where care is needed is when adding water to the nitrated liquid, great precautions being then necessary to avoid rise of temperature.



(a) Two grams of toluene require for nitration 4.39 grams of potassium nitrate. One per cent. of this—0.0439 gram—remaining unused, represents 1 per cent. of impurity in the toluene. 0.004522 Gram of potassium nitrate gives 1 c.c. of gas in the nitrometer; 0.0439 gram therefore represents 9.72 c.c. Working with 2 grams of toluene, 9.72 c.c. of gas in the nitrometer at *N.T.P.* represent 1 per cent. of impurity.

(b) Five grams of potassium nitrate are used to nitrate 2 grams of toluene, but only 4.3956 grams are required. This is an excess of 0.6044 gram, which in the nitrometer would give 133.65 c.c. of gas.

(c) Two grams of toluene give 3.95 grams of dinitrotoluene. One per cent. of this—0.0395 gram—as a deficit in the yield, represents 1 per cent. of impurity in the toluene.

Examples of Nitration. (a) *Estimation by Nitrometer.*—Two grams of toluene were nitrated with 5 grams of potassium nitrate. The liquid was made up to 150 c.c., and 15 c.c. were taken for the nitrometer estimation. (The 15 c.c. were measured from a small burette into the cup of the nitrometer, and 10 c.c. of pure sulphuric acid were used to liberate the gas.) 19.8 C.c. of gas at 16° were obtained, or 18.71 at *N.T.P.* For the whole 150 c.c. this was 187.1 c.c.; deducting the known excess used, namely, 133.65 c.c., leaves 53.45 c.c. As 9.72 c.c. represent 1 per cent. of impurity, 53.45 c.c. represent 5.5 per cent. of impurity.

The following are the results of other estimations:

Pure toluene.	Good toluene.	Poor toluene.
150 c.c. liquid, 15 c.c. taken.	175 c.c. liquid, 20 c.c. taken.	150 c.c. liquid, 15 c.c. taken.
13.27 c.c. gas at N.T.P.	15.7 c.c. gas at N.T.P.	18.64 c.c. gas at N.T.P.
For 150 c.c. liquid, 132.7 c.c.	For 175 c.c. liquid, 137.37 c.c.	For 150 c.c. liquid, 186.4 c.c.
From excess taken 133.6	From excess 133.65	From excess 133.6
-0.9 c.c.	3.72 c.c.	52.8 c.c.
- 0.9/9.72 = - 0.1 per cent.	3.72/9.72 = 0.38 per cent.	52.8/9.72 = 5.4 per cent.
Toluene 100.1 per cent.	Toluene 100 - 0.38 = 99.62 per cent.	Toluene 100 - 5.4 = 94.6 per cent.

The sample of pure toluene shows more than 100 per cent.; this is due to experimental loss. It will be realised that if the potassium nitrate is not pure and dry, or if there is any loss before the filtrate is made up to a definite volume, less nitric acid is found, and this is indicated as a small increase in the percentage of toluene.

(b) *Estimation by Weighing the Solid.*—The solid dinitro-compound is transferred from the filter funnel to a watch-glass and set in a desiccator over sulphuric acid, or the watch-glass may be set over a beaker of boiling water, when the solid melts to a clear liquid with water beneath it. On cooling, the solid forms a firm mass, from which water is readily removed by filter paper; then, after a much shorter time in the desiccator, the weight becomes constant.

It was found that when the volume, after nitration, was made up to 150 c.c., approximately 0.11 gram of solid remained in solution, and this amount is added to the weight found in the following examples.

Two grams of "pure" toluene gave 3.8337 grams of solid; adding 0.11 gram, the total dinitro-compound was 3.9437 grams; 100 per cent. toluene should give 3.9564 grams, therefore the deficit is 0.0127 gram. 0.0395 Gram deficit represents 1 per cent. of impurity, and 0.0127 gram 0.32 per cent. The toluene was therefore 100 - 0.32 = 99.68 per cent.

Two grams of a poor sample of toluene gave a deficit of 0.2573 gram, that is, 0.2573/0.0395 = 6.5 per cent. The toluene was therefore 100 - 6.5 = 93.5 per cent.

Estimation of Toluene by Miscibility with Acetic Acid.

Whilst engaged on this investigation, a report by Professor Orton was received describing the experimental work detailed in his recent paper (this vol., p. 1055). He there showed that when

88 to 90 per cent. acetic acid is mixed with toluene in the proportions of 1 c.c. of acid to 0.8 c.c. of toluene, two layers are formed, and on raising the temperature, a point of complete miscibility is reached which is definite for the same strength of acid, and so sharply defined that it can be read to one-tenth of a degree. He showed also that the temperature of miscibility of toluene rises regularly with the dilution of the acetic acid, and further, that for a given strength of acid the temperature of miscibility of toluene containing paraffin rises in direct proportion to the amount of paraffin present.

Working with two strengths of acetic acid, 87.9 and 89.5 per cent., and using pipettes of certain volumes, he prepared curves from which the percentage of a mixture of toluene and paraffin could be found when the temperature of miscibility with one of these acids had been determined. The method is susceptible of great accuracy, but it is very troublesome to prepare acetic acid of a definite strength, and almost impossible to keep a concentrated acid without absorption of moisture from the air, and, moreover, it requires so much care to carry out the process as set down by Professor Orton that it could scarcely be used as a commercial test. The following modification, consisting in the changing of an absolute to a comparative method, may, however, be carried out in any commercial laboratory.

A quantity of concentrated acetic acid of unknown strength is taken, and with equal volumes of this, the temperatures of miscibility with equal volumes of pure toluene, toluene with 5 per cent. of paraffins, and the sample of toluene to be tested, are found. Then, since the percentage of paraffins is proportional to the increase in the temperature of miscibility, the comparison of the rise of temperature of miscibility of the sample with that of the 5 per cent. paraffin mixture gives the paraffin content of the sample.

To carry out the test, there is required:

- (1) A quantity of pure toluene, which need not be synthetically pure, but might be considered as 100 per cent. quality.
- (2) A mixture of this toluene with 5 per cent. of paraffins, made by mixing 95 grams of toluene with 5 grams of paraffins of the same boiling point, prepared by the distillation of petrol.
- (3) Acetic acid, prepared by taking 100 grams of glacial acetic acid, adding a few c.c. of water, and, by trial with toluene in the proportions described below, finding if two layers are formed and if the temperature of miscibility is somewhere between 25° and 30°.
- (4) The sample to be tested.

The proportions of acetic acid and toluene found by Professor

Orton as suitable for the test may be adhered to, and two pipettes prepared, one delivering 1 c.c. and the other 0.8 c.c., or quantities in these proportions, but they need not be exact. The pipettes are made from narrow glass tubing, and must have fine capillary points to deliver very slowly. A test-tube 1.2 cm. in diameter serves as a vessel in which the miscibility point is determined, and while the test is being made it may for convenience be fixed to the thermometer by a rubber band. The test is carried out as follows. With the larger pipette, acetic acid is run into the test-tube, and pure toluene is added from the smaller pipette. The tube is then fixed to the thermometer, which must be graduated in tenths of a degree. Water is heated in a beaker holding about 2 litres, the temperature being raised speedily, and by stirring with the thermometer and tube, an approximation to the miscibility point is found by noting the temperature when the two layers disappear and a homogeneous liquid is obtained.

A little cold water is then added to the beaker, the flame is turned very low, the water thoroughly stirred, and as the temperature slowly rises, the thermometer and tube are moved continuously in the water. As the miscibility point is approached, the two layers disappear, the liquid becomes opalescent, and then suddenly becomes transparent. This is the point at which the temperature is noted. By cooling the water in the beaker 1° , the test may be repeated.

The same procedure is gone through with the 95 per cent. toluene and with the sample being examined, the tube being washed out thoroughly each time and dried in an air-oven. The following are results obtained:

	Pure toluene.	95 Per cent. toluene.	Sample.
(1) The miscibility temperature was	32.0°	38.3°	41.4°
(2) Same sample on another day, the acid being different	33.4	40.3	44.0

From (1) $38.3^{\circ} - 32^{\circ} = 6.3^{\circ}$, and $41.4^{\circ} - 32^{\circ} = 9.4^{\circ}$. A rise of 6.3° represents 5 per cent. of impurity, 9.4° represents 7.4 per cent.

From (2) $40.3^{\circ} - 33.4^{\circ} = 6.9^{\circ}$, and $44.0^{\circ} - 33.4^{\circ} = 10.6^{\circ}$. A rise of 6.9° represents 5 per cent. of impurity, 10.6° represents 7.6 per cent.

It is seen that the strength of the acid does not require to be known: it has only to remain constant during the time that three portions are withdrawn, and the pipettes do not require to be of any definite volume, although they must deliver precisely the same volume each time.

The three tests might be carried out simultaneously by having three test-tubes attached to the thermometer, one with each mixture,

1372 BAXTER AND FARGHER: 1:3-BENZODIAZOLEARSINIC

and the three points of miscibility determined as the temperature of the water is raised.

When the same sample of toluene was tested by the different methods, the following results were obtained:

From specific gravity curve	92.3 per cent.
From nitrometer estimation after nitration	92.9 "
By weighing dinitro-compound	92.6 "
By temperature of miscibility with acetic acid	92.5 "

Conclusions.—The specific gravity of commercial toluene gives a fair indication of the amount of impurity present; the estimation of the temperature of miscibility with acetic acid is quickly done, and, although a comparative method, if skilfully carried out is trustworthy; the nitration and estimation of the excess of nitric acid by the nitrometer is believed to be the most accurate test and indicates the total nitration which has taken place, and the weighing of the solid after nitration gives the actual practical yield of nitro-compound.

By none of the methods, under ordinary conditions of working, can an accuracy closer than one-half per cent. be expected.

THE TECHNICAL COLLEGE,
DUNDEE.

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CXXIX.—1:3-Benzodiazolearsinic Acids and their Reduction Products.

By ROBERT REGINALD BAXTER and ROBERT GEORGE FARGHER.

SINCE the discovery of salvarsan (Ehrlich and Berthelm, *Ber.*, 1912, 45, 756), many attempts have been made to prepare derivatives or closely allied products which would render unnecessary the somewhat elaborate technique involved in the clinical use of the original compound, which, owing to its pronounced acidity, has to be converted into the disodium salt, in turn alkaline in reaction, before use. Neosalvarsan, the sodium *N*-methylenesulphinate of salvarsan, introduced to avoid these difficulties, possesses many advantages, such as ready solubility and neutral reaction, but, in spite of these, there is a consensus of opinion in favour of salvarsan, as its spirochæticidal action appears to be stronger and more certain.

In this and in other cases the attempts have led to the formation of acid derivatives giving neutral salts with alkalis. The authors desired, on the other hand, to obtain hydrochlorides soluble in water and sufficiently less acid in reaction than salvarsan to admit

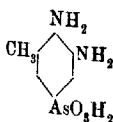
of their direct use, and it was with this object in view that the present investigation was commenced, since it was considered probable that the hydrochlorides of the arsenobenzenes derived from 1:3-benzodiazole (benzoglyoxaline) would fulfil these requirements. Further, considering the properties of the glyoxaline nucleus, they might be expected to exert acidic as well as basic properties, and thus closely resemble salvarsan itself.

Additional interest would attach to such compounds in view of their relationship to 3:4:5:3':4':5'-hexa-aminoarsenobenzene and its *N*-methyl derivatives (D.R.-P. 286667, 286668, 286854, 286855, 294276; E.P. 7488 and 8041 of 1913; U.S.P. 1081079; Benda, *Ber.*, 1914, **47**, 1316; Karrer, *Ber.*, 1916, **49**, 1448), which are stated to possess the unexpected property of dissolving in alkali hydrogen carbonates, forming carbamates with the same degree of alkalinity as that of normal blood serum and a relatively low toxicity (D.R.-P. 269660; E.P. 1667 of 1914).

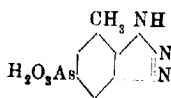
So far as the authors are aware, the benzodiazolearsinic acids have not been examined, Bertheim (*Ber.*, 1911, **44**, 3092), who described 3:4-diaminophenylarsinic acid and several of its derivatives, making no mention of them. They are, however, readily obtained by the well-known reaction of ortho-diamines with formic or acetic acid, whereby the acyl derivative first formed suffers loss of a molecule of water if a monoacyl, or of a molecule of acid if a diacyl derivative, with consequent closing of the ring (compare Ladenburg, *Ber.*, 1875, **8**, 677; Wundt, *Ber.*, 1878, **11**, 826).

The comparative stability of 3:4-diacetylaminophenylarsinic acid, which crystallises from boiling water unchanged, and does not alter save for slight decomposition when heated at 250°/20 min., and, generally, the stability of diacyl-*o*-diamines (compare Bistrzycki and Ulfers, *Ber.*, 1890, **23**, 1876), seems to indicate that in the absence of anhydrides the reaction proceeds with intermediate formation of a monoacyl derivative.

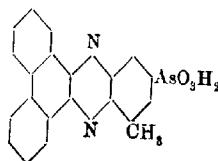
5:6-Diamino-*m*-tolylarsinic acid (I), which, together with 3:4-diaminophenylarsinic acid (Bertheim, *loc. cit.*), formed the starting material for the investigation, was obtained by the reduction of 5-nitro-6-amino-*m*-tolylarsinic acid (this vol., p. 989) with sodium hyposulphite. It undergoes all the condensations typical of an



(I)



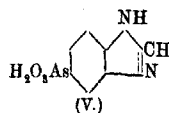
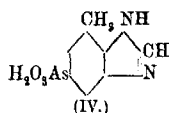
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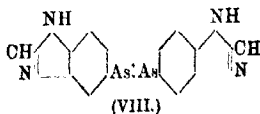
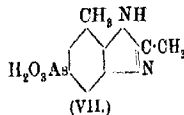
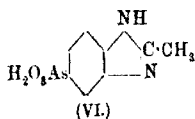
(III.)

o-diamine, giving, for example, with sodium nitrite in acid solution, 7-methyl-1:2:3-benzotriazole-5-arsinic acid (II), and with phenanthraquinone, 4-methylphenanthraphenazine-2-arsinic acid (III). The latter derivative shows the colour reactions characteristic of phenanthraphenazine.

With boiling glacial formic acid, the acids readily yielded 7-methyl-1:3-benzodiazole-5-arsinic acid (IV) and 1:3-benzodiazole-5-arsinic acid (V) respectively.



The action of acetic acid did not proceed quite so smoothly. 3:4-Diaminophenylarsinic acid, although stated (Bertheim, *loc. cit.*) to be readily soluble in acetic acid, is far from being so, and, on boiling with acetic acid, acetic anhydride, or a mixture of the two, gives rise to very highly coloured products, which are difficult to purify. If the reaction is carried out as described in the experimental portion of this paper, the main product is 3:4-diacetylaminophenylarsinic acid, which, on heating with water in a sealed tube at 130°, yields 2-methyl-1:3-benzodiazole-5-arsinic acid (VI). In the case of the higher homologue, the desired reaction takes place predominantly, with the formation of 2:7-dimethyl-1:3-benzodiazole-5-arsinic acid (VII). Incidentally, it may be mentioned that it has since been found that if 3:4-diaminophenylarsinic acid, dissolved in the requisite amount of sodium hydroxide (40 per cent. solution) to form the monosodium salt, is treated with sufficient acetic anhydride to neutralise the sodium hydroxide and form acetic acid with the water present, and then boiled, the main product of the reaction is the benzodiazole derivative.



The reduction of the above acids with hypophosphorous acid, although it proceeds normally, leads to gelatinous products difficult

to handle, and consequently the reduction was carried out by means of sodium hyposulphite. This gives pale yellow *arsenobenzenes*, insoluble in water, which were converted into hydrochlorides by precipitating their solutions in acetic acid with excess of hydrochloric acid, or by treating the suspensions of the bases in water with just sufficient hydrochloric acid to bring about solution, and precipitating as before. The *hydrochlorides* form pale yellow powders, soluble in water, but very sparingly so in the usual organic solvents. Their aqueous solutions react strongly acid to litmus, but neutral to methyl-orange.

It was expected that this acidity would prove too great for purposes of intravenous injection, and that it would be difficult to distinguish between the effect due to the acidity and that due to the arsenic compound. This was confirmed by experiments with 5:5'-*arseno-1:3:1':3'-benzodiazole* (VIII) by Miss Soref, of the Wellcome Physiological Research Laboratories.

EXPERIMENTAL.

3:4-Diaminophenylarsinic Acid.

The preparation of considerable quantities of this acid was carried out according to the directions given by Berthelm (*loc. cit.*), save that it was found advisable to omit the boiling of the solution after the reduction with sodium hyposulphite, as this diminished the yield and gave a more highly coloured product.

1:3-Benzodiazole-5-arsinic Acid (V).

Ten grams of 3:4-diaminophenylarsinic acid were boiled under reflux condenser for six hours with 100 c.c. of glacial formic acid. After removal of the excess of formic acid by distillation, water was added, when 7.5 grams of crystalline material rapidly separated. To remove adhering traces of colouring matter, the product was treated with charcoal in dilute alkaline solution. On making neutral to methyl-orange, crystallisation commenced at once, practically the whole being recovered in a pure state.

1:3-Benzodiazole-5-arsinic acid crystallises from water, in which it is sparingly soluble, in clusters of minute, flattened prisms, which are anhydrous. On heating, it gradually darkens above 250° and decomposes rapidly about 297° (corr.).

Found: N = 11.4; As = 30.8.

$C_7H_7O_3N_2As$ (242.1) requires N = 11.6; As = 30.96 per cent.

5:5'-Arseno-1:3:1':3'-benzodiazole (VIII).

A solution of 5 grams of 1:3-benzodiazole-5-arsinic acid in 100 c.c. of water containing 1.2 grams of sodium hydroxide was treated with 50 grams of sodium hyposulphite and 11.5 grams of magnesium chloride dissolved in 300 c.c. of water, and the mixture heated, with stirring, at 60° for two hours in an atmosphere of carbon dioxide, by which time the precipitation of the yellow arsenobenzene was complete. After cooling, the product was collected, well washed with water, suspended in 90 c.c. of water, dissolved by the addition of sufficient hydrochloric acid to form the dihydrochloride, filtered from traces of undissolved matter, and precipitated by pouring into an equal volume of concentrated hydrochloric acid. The hydrochloride was collected, well washed with alcohol and ether, and dried in a vacuum over sulphuric acid. The yield amounted to 3.9 grams.

5:5'-Arseno-1:3:1':3'-benzodiazole is obtained as a bright yellow powder practically insoluble in water or the usual organic solvents, sparingly, if at all, soluble in methyl alcohol containing hydrochloric acid, but fairly readily so in 50 per cent. acetic acid. The dihydrochloride forms a pale yellow powder soluble in water, very sparingly so in methyl alcohol or ethyl alcohol, and quite insoluble in acetone or ether. The aqueous solution reacts acid to litmus, but neutral to methyl-orange. After drying in a vacuum overnight, it retains solvent equivalent to two molecules of water.

Found: N=11.3; As=30.2; Cl=13.8.

$C_{11}H_{10}N_4As_2 \cdot 2HCl \cdot 3H_2O$ (493.1) requires N=11.4; As=30.4; Cl=14.4 per cent.

3:4-Diacetylaminophenylarsinic Acid and 2-Methyl-1:3-benzodiazole-5-arsinic Acid (VI).

Experiments in which diaminophenylarsinic acid was heated with glacial acetic acid, with acetic anhydride, with acetyl chloride and pyridine, or with acetic anhydride in the presence of a trace of sulphuric acid, were unsuccessful, owing to the considerable amount of decomposition which occurred. It was found, however, that if the acid, dissolved in methyl alcohol, was treated with a mixture of acetic acid and acetic anhydride, and the methyl alcohol then removed as completely as possible by distillation on the water-bath, the resulting solution, after heating to active boiling for four hours, gave an excellent yield of a product, which, from its composition, proved to be the diacetyl derivative of diaminophenylarsinic acid.

3:4-Diacetylaminophenylarsinic acid crystallises from water, in

which it is fairly readily soluble, as a felted mass of fine needles which retain from 2 to 2.5 per cent. of solvent.

Found: loss at 110° (two specimens) 2.6, 2.2.

In dried material: $N=8.8$; $As=23.8$.

$C_{10}H_{13}O_3N_2As$ (316.1) requires $N=8.9$; $As=23.7$ per cent.

As the product did not lose acetic acid when heated to $250^{\circ}/20$ mm., it was heated with ten times its weight of water in a sealed tube for four hours at 130° , when the desired reaction took place almost completely.

2-Methyl-1:3-benzodiazole-5-arsinic acid crystallises from water, in which it is somewhat sparingly soluble, in minute needles containing two and a-half molecules of water of crystallisation, the last half molecule being removed with difficulty at 110° , but fairly readily at 120° . After drying at 110° , it darkens on heating above 250° and decomposes at about 270° (corr.).

Found: loss at $110^{\circ}=15.5$.

$C_8H_9O_3N_2As \cdot 2\frac{1}{2}H_2O$ requires $H_2O=15.0$ per cent.

In dried material: $C=37.3$; $H=3.8$; $N=10.7$; $As=29.3$.

$C_8H_9O_3N_2As$ (256.1) requires $C=37.5$; $H=3.5$; $N=10.9$; $As=29.3$ per cent.

2:2'-Dimethyl-5:5'-arseno-1:3:1':3'-benzodiazole.

This was prepared in the same manner as 5:5'-arseno-1:3:1':3'-benzodiazole, which it resembles very closely in its properties.

The *dihydrochloride* forms a pale yellow powder, soluble in water, but almost completely insoluble in methyl alcohol, ethyl alcohol, ether, or acetone. After drying in a vacuum for twenty-four hours, it retains solvent approximating to three molecules of water. In aqueous solution it reacts acid to litmus but neutral to methyl-orange.

Found: $N=10.3$; $Cl=12.7$; $As=28.0$.

$C_{16}H_{14}N_4As_2 \cdot 2HCl \cdot 3H_2O$ (539.1) requires $N=10.4$; $Cl=13.1$;

$As=27.8$ per cent.

5:6-Diamino-m-tolylarsinic Acid (I)

A solution of 8.6 grams of 5-nitro-6-amino-*m*-tolylarsinic acid in 75 c.c. of water and 6.2 c.c. of 10*N*-sodium hydroxide was cooled to -1° and treated, in one operation, while stirring vigorously, with 20.4 grams of sodium hyposulphite. When the reaction was complete, as shown by the change in colour, the solution was filtered, treated with 8.1 c.c. of hydrochloric acid (D 1.12), and the resulting acid, which separated in the course of a few minutes,

collected, washed with water, and recrystallised from water, in which it is sparingly soluble in the cold, but fairly readily so on warming. It separates in colourless needles, which contain between one and a-half and two molecules of water of crystallisation. It dissolves fairly readily in methyl alcohol or acetic acid, but is very sparingly soluble in ether, benzene, or petroleum. Its solution in dilute hydrochloric acid gives a characteristic, deep violet coloration with a drop of a dilute solution of potassium dichromate. It appears to decompose slowly on keeping.

Loss at $110^{\circ} = 11.2$.

$C_7H_{11}O_3N_2As.1\frac{1}{2}H_2O$ requires 9.9 per cent.

$C_7H_{11}O_3N_2As.2H_2O$ requires 12.8 per cent.

In dried material: $N=11.3$; $As=30.4$.

$C_7H_{11}O_3N_2As$ (246.1) requires $N=11.4$; $As=30.5$ per cent.

7-Methyl-1:2:3-benzotriazole-5-arsinic acid (II) was obtained by treating a solution of 3:4-diamino-*m*-tolylarsinic acid in dilute hydrochloric acid with a molecular proportion of sodium nitrite. It forms a crystalline powder very sparingly soluble in water, but more readily so in alcohol. It crystallises from 50 per cent. alcohol in minute, colourless, glistening needles, which are anhydrous, and gradually decompose on heating above 280° .

Found: $N=16.6$.

$C_7H_9O_3N_3As$ (257.1) requires $N=16.4$ per cent.

4-Methylphenanthraquinazoline-2-arsinic acid (III) was obtained by the condensation of molecular proportions of phenanthraquinone and 3:4-diamino-*m*-tolylarsinic acid in acetic acid solution. It forms an amorphous, yellow powder, sparingly soluble in water and the usual organic solvents. With concentrated sulphuric acid, it develops an eosin-red colour, with nitric acid a cherry-red, and with hydrochloric acid an insoluble red compound. The colour is discharged in all three cases by dilution with water. It dissolves in dilute sodium carbonate or sodium hydroxide, but a flocculent precipitate of the sodium salt is thrown down on the addition of excess of the reagent.

Found: $N=6.4$.

$C_{21}H_{15}O_3N_3As$ (418.2) requires $N=6.7$ per cent.

7-Methyl-1:3-benzodiazole-5-arsinic Acid (IV).

Two grams of 3:4-diamino-*m*-tolylarsinic acid were boiled with 20 c.c. of glacial formic acid for six hours. The isolation of the product was carried out as in the case of 1:3-benzodiazole-5-arsinic acid, save that the treatment with charcoal was found to be more

effective in acid solution. The air-dried product contains only traces of moisture and resembles the lower homologue very closely in its properties. It dissolves sparingly in water and crystallises in minute, prismatic needles, which darken when heated above 280° and melt and decompose at about 300° (corr.).

Found: loss at $110^{\circ}=1.3$.

In dried material: N=10.8; As=29.4.

$C_8H_5O_3N_2As$ (256.1) requires N=10.9; As=29.3 per cent.

7:7'-Dimethyl-5:5'-arseno-1:3:1':3'-benzodiazole.

This was obtained by the reduction of the above acid with sodium hyposulphite in the manner previously described (p. 1376), as a pale yellow powder, insoluble in water and the usual organic solvents, but moderately soluble in acetic acid. The corresponding *dihydrochloride* forms a pale yellow, granular powder soluble in water, but insoluble in methyl alcohol, ethyl alcohol, ether, or acetone. After drying for twenty-four hours under greatly reduced pressure, it retained solvent corresponding with two molecules of water.

Found: N=10.6; As=28.6; Cl=13.1.

$C_{10}H_{14}N_4As_2 \cdot 2HCl \cdot 2H_2O$ (521.1) requires N=10.75; As=28.8; Cl=13.6 per cent.

2:7-Dimethyl-1:3-benzodiazole-5-arsinic Acid (VII).

This acid was obtained by the prolonged action (six to eight hours) of boiling acetic acid on 5:6-diamino-*m*-tolylarsinic acid, the isolation being carried out in the usual manner. It is somewhat soluble in boiling water, but sparingly so in cold, and separates from the former in minute, prismatic needles which contain two molecules of water of crystallisation.

Found: loss at $110^{\circ}=12.2$.

$C_9H_{11}O_3N_2As \cdot 2H_2O$ requires 11.8 per cent.

In dried material: N=10.6; As=27.9, 27.5.

$C_9H_{11}O_3N_2As$ (270.1) requires N=10.4; As=27.75 per cent.

2:7:2':7'-Tetramethyl-5:5'-arseno-1:3:1':3'-benzodiazole.

The above acid was readily reduced to the corresponding *arsenobenzene* by sodium hyposulphite, under the conditions previously employed. The *arsenobenzene* closely resembles those already described in its physical and chemical properties. The *dihydrochloride* forms a pale yellow powder soluble in water, but insoluble

in the usual organic solvents. After drying for twenty-four hours in a vacuum, it retains solvent corresponding with approximately two molecules of water.

Found: N=10.0; As=27.3; Cl=12.3.

$C_{18}H_{18}N_4As_2 \cdot 2HCl \cdot 2H_2O$ (549.1) requires N=10.2; As=27.3;
Cl=12.9 per cent.

WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C. 1.

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CXXX.—*The Equilibrium between Carbon, Hydrogen, and Methane.*

By HUBERT FRANK COWARD and STANLEY PIERCE WILSON.

EQUILIBRIUM in the system $C + 2H_2 = CH_4$ is more suited to experimental study, in one respect, than the more commonly investigated high-temperature dissociations, such as those of water, carbon dioxide, and hydrogen chloride. The proportion of methane in equilibrium with carbon and hydrogen diminishes with increasing temperature, and hence when equilibrium is once established in the zone of reaction, the cooling of the gaseous mixture on its removal from the carbon is not accompanied by an alteration in composition. It is a simple matter to ensure the absence of elementary carbon from any but the zone of measured temperature in which the equilibrium is attained.

The synthesis of methane from its elements was achieved by Bone and Jerdan (T., 1897, **71**, 41; 1901, **79**, 1042), who found that when a stream of hydrogen was passed over carbon at about 1200°, the resulting gaseous mixture was hydrogen containing, roughly, 1 per cent. of methane and no other hydrocarbon. This synthesis was confirmed by Bone and Coward (T., 1910, **97**, 1219), who obtained an almost theoretical yield of methane from 0.0824 gram of carbon.

The decomposition of methane into carbon and hydrogen, without the permanent formation of any detectable amount of any other hydrocarbon, was demonstrated by Bone and Coward (T., 1908, **93**, 1197).

The above-mentioned experiments, the forerunners of those now to be described, indicated that the equilibrium mixture at 1000–1200° contained, roughly, 1 per cent. of methane.

The determination of equilibrium values in the system has been

attacked in two other quarters. Mayer and Altmayer (*Ber.*, 1907, 40, 2134) carried out experiments with the aid of a catalyst at temperatures ranging from 475° to 625°, and declared that Bone and Jerdan's methane formed at 1200° could not have arisen by the direct union of carbon and hydrogen. Pring (*T.*, 1910, 97, 498) found that a carbon rod lightly coated with platinum gave the value 0.55 per cent. of methane in equilibrium at 1200° and 0.30 per cent. at 1500°. Finally, Pring and Fairlie (*T.*, 1912, 101, 91) conducted experiments under high pressures, and, assuming the law of mass action to hold down to atmospheric pressure, calculated the following equilibrium values:

	Amorphous carbon.	Graphite.
1200°	0.36 per cent. of methane	0.24 per cent. of methane
1500°	0.21 " "	0.07 " "

The series of experiments, the results of which are recorded below, were conducted in essentially the same way as those described in detail by Bone and Coward (*loc. cit.*), except that the gaseous products of reaction were passed backwards and forwards over the carbon used until analysis showed the attainment of constancy of composition. The porcelain tube used to contain the reacting substances was, as before, set up coaxially with a wider one, through which dry hydrogen was passed. The wider tube was heated electrically by means of a platinum wire resistance. The temperature of the inner tube was, at 1100°, constant, within $\pm 6^\circ$, for a length of 10 to 15 cm. (in different furnaces), which was ample to contain the carbon used. The latter was held in a quartz boat or in an open quartz tube just narrow enough to pass freely to the porcelain tube.

The temperature of the reaction was measured by means of a platinum and platinum-rhodium thermo-junction lying in the inner porcelain tube, but encased in a thin quartz tube; one wire was insulated from the other by running it through a fine quartz tube. The thermo-couple was standardised by means of thium chloride (m. p. 605°), antimony (m. p. 628°), an alloy of 9 per cent. of copper and 20 per cent. of tin (m. p. 738°), potassium carbonate (m. p. 835°), and electrolytic copper (m. p. 1084°).

The gaseous products were collected direct from the furnace over a mixture of glycerol and water, and before being re-passed into the furnace were dried by passage through a U-tube containing fragments of dry stick potassium hydroxide.

The electrolytic hydrogen and the carbon were prepared as described by Bone and Coward. The methane was obtained by interaction between aluminium carbide and water, washed with

ammoniacal cuprous chloride and sulphuric acid, and collected after air had been displaced from the apparatus used for the preparation. Hydrogen was then removed by liquefaction of the gas by means of liquid air, and subsequent distillation. This procedure was proved to afford a satisfactory means for removing hydrogen from large volumes of methane. It cannot, however, be recommended for removing air from methane; methane must be prepared free from air in the first place unless large quantities of the gas are sacrificed during the fractional distillation after liquefaction.

Experiments at 1100°.

Synthesis of Methane.—Pure dry hydrogen was passed over 1 gram of carbon (ash, 0.06 per cent.) at the rate of about 1 litre per hour until from 5 to 6 litres of gas had been collected. A litre of this was measured and treated with palladium foil; the resulting concentrate was measured and analysed. The residual 4 to 5 litres of the gas, once passed over carbon, were re-passed at the same rate as before, and a sample was taken for analysis after concentration. The residual gas was then passed twice again over the heated carbon, and again sampled for analysis. The results of the analysis, calculated back to the unconcentrated mixtures, are (in percentages):

	1st passage.	2nd passage.	3rd passage.
Carbon monoxide	0.07	0.16	0.51
Methane	0.46	0.70	0.65
Nitrogen	0.21	0.51	0.87

The experiment was repeated with the same sample of carbon:

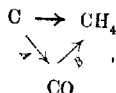
	1st passage.	2nd passage.	3rd passage.	4th passage.
Carbon monoxide	0.13	0.23	0.32	0.47
Methane	0.43	0.68	0.64	0.67
Nitrogen	0.26	0.49	0.56	0.69

Each experiment shows an accumulation of methane during the first and second passage of the gas over the carbon, but thenceforth the methane content remained practically constant.

The nitrogen content is a measure of the leaking in of air during the experiment and analysis, and in itself is unimportant. The carbon monoxide, due in part to air and in part to a slight oxidising action by the glaze of the heated tube, raises the question as to whether carbon monoxide may play some important part in the synthesis. It is just conceivable, although contrary to the results of other investigations,* that carbon monoxide would be

* Bone and Coward (T., 1908, 93, 1937) showed that when a mixture of 98 per cent. of hydrogen and 2 per cent. of carbon monoxide was passed through a porcelain tube at 1100° in the absence of carbon, no more than 0.02 per cent. of methane was present in the issuing gas.

reduced by the large excess of hydrogen present to methane and water; the latter would regenerate carbon monoxide by reaction with carbon. If carbon monoxide acted as a catalyst in the synthesis, then the two reactions—whatever they might be precisely—indicated as *A* and *B* in the scheme



would each be fast in comparison with the rate of the direct synthesis. Hence the accumulation of carbon monoxide exhibited in the experiments would only be possible provided that the reversion of methane to carbon and hydrogen were a very rapid reaction indeed when the methane was increased above about 0.7 per cent. That this is not the case is shown by experiments (below) on the decomposition of methane at 1100°. The carbon monoxide is therefore produced as a side reaction between carbon and water vapour, and plays no part in the formation of at least the great proportion of the methane found.

Decomposition of Methane.—A mixture containing 2.0 per cent. of methane and 98.0 per cent. of hydrogen was passed over the same sample of carbon, eight times in all. The gas was sampled from time to time for analysis as before. The results were (in percentage):

	2nd passage.	5th passage.	8th passage.
Carbon monoxide	0.45	0.65	0.92
Methane	1.18	0.64	0.61
Nitrogen	0.49	0.52	1.04

Here, again, the steady formation of carbon monoxide is evident, whilst the methane-content becomes constant at or before the fifth passage, and shows the attainment of equilibrium, as in the synthetic experiments.

Synthesis and Decomposition of Methane in the Presence of Nickel.—One gram of the pure carbon was intimately mixed with 1 gram of nickel oxide, obtained by igniting the nitrate, and the mixture heated to 300° in hydrogen until no more water vapour was formed, and then raised gradually to 1100° in a current of hydrogen. The gas issuing from the tube was collected and re-passed three times; analysis showed it to contain: carbon monoxide=1.29, methane=0.61, nitrogen=0.49 per cent.

The decomposition of methane was conducted with a mixture containing 5.7 per cent. of methane and 94.3 per cent. of hydrogen. After five passages over the same mixture of carbon and nickel, the gas contained: carbon monoxide=1.27, methane=0.57, nitrogen=

1.33 per cent. The increase in carbon monoxide is ascribed to the well-known difficulty of reducing finely divided nickel oxide completely in hydrogen.

Collection of Results at 1100°.—The equilibrium values indicated above are:

	Pure carbon.	Carbon-Nickel mixture.
Synthesis	(i) 0.65; (ii) 0.67	0.61
Decomposition	0.61	0.57

The mean value for the equilibrium amount of methane at 1100° is therefore 0.62 per cent.

Experiments at 1000°.

Synthesis of Methane.—The synthesis of methane from the highly purified carbon used in the experiments at 1100° proved to be too slow for the attainment of equilibrium at 1000°. A less pure sample containing 0.5 per cent. of incombustible matter (silica) gave the following percentage results in an experiment conducted in a similar manner to the corresponding experiment at 1100°.

	1st passage.	2nd passage.	3rd passage.	4th passage.
Carbon monoxide	0.05	0.10	0.17	0.28
Methane	1.06	0.97	0.96	1.06
Nitrogen	0.15	0.44	0.32	0.31

Equilibrium is evidently established from the first. The carbon monoxide-content is much lower than in the experiments at 1100° and although increasing throughout, has no appreciable influence on the methane content of the gases. The high value for nitrogen in the second experiment is most probably due to a small in-leakage of air during the concentration of the sample of gas analysed.

An experiment with 1 gram of carbon containing 4 per cent. of platinum, finely disseminated, gave similar values:

	1st passage.	2nd passage.
Carbon monoxide	0.07	0.16
Methane	1.09	1.08
Nitrogen	0.09	0.19

Decomposition of Methane.—A mixture containing 2.0 per cent. of methane and 98.0 per cent. of hydrogen gave in two separate experiments:

	First experiment.		Second experiment.
	3rd passage.	5th passage.	2nd passage.
Carbon monoxide	0.19	0.41	0.55
Methane	1.16	1.13	1.06
Nitrogen	0.83	0.84	0.69

Synthesis and Decomposition of Methane in Presence of Nickel.

—The same sample of a carbon-nickel mixture as was used for the experiments at 1100° gave the following results at 1000°. Starting with pure hydrogen, samples of the unconcentrated gases showed on analysis an approximately constant content of methane from the second to the sixth passages. The methane then present was determined accurately after concentration of the mixture: carbon monoxide=2.2, methane=1.23, nitrogen=0.7 per cent. The decomposition of a 3.7 per cent. methane mixture gave, in similar circumstances, a constant content of methane from the third to the seventh passage. The final composition was: carbon monoxide=1.1, methane=1.18, nitrogen=1.2 per cent.

Collection of Results at 1000°.—The equilibrium values indicated above are:

	Carbon (0.5 per cent. of ash).	Carbon-4 per cent. of platinum.	Carbon-Nickel.
Synthesis	1.01	1.09	1.23
Decomposition	1.13; 1.06	—	1.18

The mean value for the equilibrium amount of methane at 1000° is therefore 1.12 per cent.

Experiments at 850°.

The reaction between carbon and hydrogen proved to be too slow at 850° for equilibrium to be reached at that temperature within a reasonable period of time in the apparatus employed. Experiments with the nickel-carbon mixture were more successful. Synthetic experiments with a slow stream of gas showed that from the sixth to the eighteenth passage the methane content remained constant, according to the approximate results of analyses of unconcentrated samples of the mixture. The methane present at the end of the eighteenth passage was determined after concentration: carbon monoxide=0.5, methane=2.60, nitrogen=1.3 per cent. Corresponding experiments on the decomposition of methane, carried out with a very slow stream of gas, showed constant composition between the second and fifth passages of the gas: carbon monoxide=0.2, methane=2.4, nitrogen=0.6 per cent.

The equilibrium amount of methane at 850° is therefore 2.5 per cent.

Experiments at 650°.

Hydrogen and methane were separately heated for prolonged periods in contact with carbon at 650°. In no case did the analyses of the resulting mixtures indicate that equilibrium could be attained within any reasonable period of time, although attempts

were made to activate the carbon by means of finely divided nickel, (a) by grinding together nickel oxide and pure carbon and reducing in hydrogen at 300°; (b) by igniting a mixture obtained by evaporating nickel nitrate in the presence of excess of finely divided carbon, and heating finally in hydrogen at 300°; (c) by absorbing nickel nitrate in small pieces of porous porcelain, igniting, and depositing carbon by the prolonged passage of methane over the heated solid.

It is not concluded that it is impossible to prepare carbon in a sufficiently active state to attain equilibrium at this temperature, but the claim of Mayer and Altmayer (*loc. cit.*) to have succeeded at still lower temperatures is much weakened by the fact that they record no attempt to discover whether their gaseous products contained carbon monoxide. If, as it seems fair to assume, therefore, they overlooked carbon monoxide, much of their so-called methane may have had no actual existence. That there must have been carbon monoxide present in their products can scarcely be doubted in view of, first, the presence of large amounts of nitrogen, and, secondly, their use of somewhat large amounts of nickel, which, as is known, is difficult to obtain free from nickel oxide by reduction of the latter at a low temperature.

Summary and Conclusions.

The percentage composition of the equilibrium mixtures of methane and hydrogen in contact with amorphous carbon at atmospheric pressure is

	1100°.	1000°.	850°.
Methane	0.6	1.1	2.5
Hydrogen	99.4	98.9	97.5

These values will doubtless be capable of correlation by means of a thermodynamical equation, when the specific heats of the three reacting substances are known, together with the heat of formation of methane. Information as to the specific heat of methane at high temperatures is, however, wanting at present, and the heat of combustion of methane has apparently not been determined with a gas of sufficient purity. Calculation of the mean value of the latter between 850° and 1100° from the experimental values for the equilibrium, by means of the integrated form of the equation

$$\frac{d \log K}{dT} = - \frac{Q}{RT^2},$$

gives the value 12,000 calories, with a possible error of perhaps a couple of thousand calories.

THE PROPERTIES OF AMMONIUM NITRATE. PART I. 1367

In conclusion, the authors wish to acknowledge their indebtedness to assistance from the Government Grant Committee of the Royal Society, to Messrs. Johnson, Matthey and Co. for the loan of palladium, and to Mr. T. R. Bradbury, M.Sc., for valuable co-operation during one period of the work.

FACULTY OF TECHNOLOGY,
MANCHESTER UNIVERSITY.

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CXXXI.—The Properties of Ammonium Nitrate. Part I. The Freezing Point and Transition-temperatures.

By REGINALD GEORGE EARLY and THOMAS MARTIN LOWRY.

AMMONIUM nitrate is remarkable amongst salts both for its easy fusibility and for the fact that the salt exists in not fewer than five crystalline forms, the ranges of stability of which are marked by a series of four well-defined transition-temperatures. These different forms are conveniently named, in the same way as the various forms of iron, by Greek letters, starting with the form which is stable at the lowest temperatures.

The crystalline forms of these modifications, and the published data in reference to the transition-temperatures, are set out in the following table.

TABLE I.

Changes of State in Ammonium Nitrate.

Form of salt.	Crystalline system.	Change of state.	Transition-temperature.
Liquid	—	—	—
ε	Cubic	ε to liq.	165—166°, 165°, 168°, 165.2°.
			127°, 124—125°, 124°, 123.5—125.5°,
		δ to ε	125.6°, 122.6°, 126.2°, 124.0—
			125.6°, 125.0°, 125.2°.
δ	*Rhombohedral	γ to δ	87°, 82.5—86°, 81°, 82.5—86.5°,
			82.8°, 83.0°, 86°, 85.5°, 84°, 84°,
			82.26°.
γ	†Rhombic	β to γ	36°, 31—35°, 35°, 31—35°, 32.4°,
β	Rhombic		32.2°, 35.0°, 35.0°, 32.5°.
α	Tetragonal	α to β	—16°, —18°.

* Or tetragonal.

† Or monosymmetric.

In view of the fundamental character of these constants and of the fact that the temperatures are all easily accessible, a redetermination was made which has had the effect of fixing the freezing

point with an estimated error of a few tenths of a degree at 169.6° , whilst the three upper transition points have been determined probably within a few hundredths of a degree at 125.2° , 84.2° , and 32.1° .

I. Freezing Point at 169.6° .

The difficulty of determining the correct melting point or freezing point of the salt, and the fact that values much below the correct figure have so often been recorded, arise from two characteristic properties of the salt, namely, the very great sensitiveness of the freezing point to the influence of small quantities of moisture (details in reference to which will be given in a later paper) and the tendency of the salt to retain its moisture even when attempts are made to remove it by somewhat drastic methods.

On account of these properties of the salt, we obtained in our earlier experiments a long series of concordant values for the freezing point, which were afterwards proved to be more than 2° too low. These freezing points were determined by observing the arrest of temperature which occurred immediately after crystallisation had begun in about 40 grams of the molten salt, the salt being stirred vigorously in a glass tube surrounded by an air-jacket in a bath of boiling water in order to prevent over-rapid cooling. The temperatures were measured by a thermometer graduated in fifths of a degree from 0° to 200° , and recently re-standardised to 0.02° at the National Physical Laboratory; this thermometer was of the compensated type, and the zero had remained constant within 0.02° over a period of about ten years. Two auxiliary thermometers were used to record the temperatures of the "exposed column" of mercury inside and outside the glass tube containing the salt. A series of freezing points determined in this way gave very concordant figures, the corrected values being as follows:

166.95° , 166.95° , 166.90° , 167.15° , 167.0° . Mean, 167.0° .

This was the freezing point of a sample of the salt which had been recrystallised twice from water and dried, first in a steam-oven during several hours, and then during a day and a night over sulphuric acid in a desiccator exhausted with the help of a Gaede mercury pump.

Doubt was first thrown on the correctness of these readings when it was discovered that a commercial sample of ammonium nitrate which had been dried and ground, and then re-dried in the usual way in the laboratory, gave a freezing point of 168.8° , that is, nearly two degrees higher than our best laboratory specimen of the salt. As this higher freezing point could obviously not be due

to impurities, which would tend to lower the freezing point of the salt, it could only be attributed to the fact that the drying had been accompanied by a grinding which was absent in the laboratory process of purification already described.

In order to secure equally favourable conditions in the laboratory, the purified salt was heated in a steam-oven, cooled, and crushed in a mortar, and left overnight in a vacuum desiccator, this cycle of operations being repeated three or four times. A series of freezing points of material prepared in this way gave the following figures:

169.16°, 169.14°, 169.04°, 169.05°, 169.06°. Mean, 169.09°.

The first two values were for ammonium nitrate from Hopkin and Williams, twice recrystallised; the next two are for the same sample after storing for some weeks in a desiccator over calcium chloride; the last value is for a commercial sample of Norwegian nitrate recrystallised from water and dried by the method just described. These experiments showed that the freezing point of the salt was at least 169.1°, and might be as high as 169.2° in view of the first two values recorded in the list.

A further improvement in the freezing point was effected by sealing up in an exhausted flask, connected with a bulb of phosphoric oxide, some of the salt prepared as described above. The nitrate was shaken up repeatedly to expose a fresh surface, and at the end of a week the freezing point was determined. In plotting the cooling curves for these determinations of the freezing point, two modifications were made in the practice previously adopted, namely, (i) the outer water-jacket was kept at 80° instead of 100° in order to reduce the amount of water vapour round the apparatus; (ii) the stirring of the molten salt was stopped as soon as the temperature showed signs of becoming steady, in order to reduce the loss of heat from the molten mass, and so to prolong as much as possible the horizontal arrest in the cooling curve. The freezing points determined in this way were

169.58°, 169.55°.

After three months' further drying by phosphoric oxide, no further rise of the freezing point was produced, but, on the contrary, it appeared to have receded slightly. The freezing point of the pure dry salt may therefore be placed at 169.6°. If the freezing point of the salt is expressed in whole numbers, the figure 170° is more exact than any hitherto given, since the experimental numbers recorded above are unlikely to be too high, but may still be slightly below the true maximum figure.

The drying of ammonium nitrate, which is not really a difficult

operation when dealing with the solid salt, cannot be effected merely by stronger heating, since the salt, which begins to decompose at 200° , retains even at this temperature the moisture produced by decomposition. Thus, two samples, which had been heated to vigorous effervescence at 225° , froze at 166.8° and 167.0° when cooled again to the freezing point of the molten salt. Again, a sample of the nitrate which melted originally at 169° , froze at 165.5° after being heated to 230° to 240° for a few minutes, and at 163.4° after a second heating. The molten salt, indeed, appears to cling to its water quite as tenaciously as concentrated sulphuric acid, and it is only by grinding the solid to a fine powder that complete drying is readily effected.

II. *Transition-temperature at 125.2° .*

When the molten salt is allowed to cool from the melting point in a tube provided with a thermometer dipping into the salt, the highest of the transition-temperatures referred to in table I gives rise only to a retardation of cooling at about 125° . In order to produce slower cooling and to secure, if possible, a horizontal arrest in the cooling curve, in spite of the poor thermal conductivity of the salt, the following method was adopted. About 90 grams of the purified salt were melted and poured into a small beaker, which was lowered into the centre of a vacuum-jacketed cylinder. A standard thermometer was inserted, and the salt was allowed to set round the bulb. The stem of the thermometer passed through a large rubber stopper, which served to close the top of the cylinder and so prevent loss of heat by convection to the outer air. The cylinder, in its turn, was immersed as far as possible in a bath of hot water, stirred mechanically, and maintained at a fairly constant temperature by a flame. A Bunsen valve was provided for the escape of air by expansion from the cylinder, whilst two auxiliary thermometers gave the temperatures of the "exposed column" of the standard thermometer. An attempt was made to retard the cooling still further by exhausting the air from the interior of the cylinder, but this procedure did not appear to serve any useful purpose, and was abandoned, because of the additional trouble caused by the frothing up of the salt to a porous mass during exhaustion. When observing the transition point at 125° , the temperature of the outer water-bath was maintained at 95° , but it was then generally allowed to cool to 75° in order to observe the further transition at 84° , to which reference is made in Section III below. The readings obtained in this way with air in the vacuum cylinder were 125.2° , 125.6° , 125.8° , 125.1° , 125.6° , 125.2° , whilst

with the air exhausted from the cylinder the readings were 125.2° and 125.4° . The mean of the whole series is 125.4° . Zawidzki (*Zeitsch. physikal. Chem.*, 1903, **47**, 721) obtained a mean value of 125.0° for arrests in the cooling of ammonium nitrate, alone and mixed with silver nitrate.

In the case of the transition point at 84° , the poor conductivity of the salt may be compensated by stirring the powder in a small revolving drum heated externally by means of a vapour-jacket, but this method cannot be employed at the higher temperatures, as the powder begins to cake into tough lumps. A much more effective method of securing good conduction during heating and cooling consists in stirring the powdered salt in a bath of liquid not differing too widely from it in density. The liquid selected for this purpose was a mixture of tribromoethane (D 2.62 ; b. p. 188°) and xylene (D 0.86 ; b. p. 140°), the density of ammonium nitrate at this temperature being about 1.6 . Good results were also obtained by using nitrobenzene (D 1.22 ; b. p. 211°). This method of improving the thermal conductivity has the advantage that the thermometric measurements can be made within a maximum of accuracy. The procedure was as follows. The liquid was made into a "mush" with powdered ammonium nitrate in a glass tube 20 cm. long and 3.7 cm. in diameter, provided with a stirrer and a split cork to carry a standard thermometer; as before, two auxiliary thermometers were used to record the temperature of the "exposed column" of mercury. The glass tube was surrounded by a metal cylinder 20 cm. long and 5 cm. in diameter, closed at the top with cotton wool, and forming a narrow air-jacket round the tube. This cylinder was supported by a bung in the axis of a larger metal cylinder, 32 cm. long and 10 cm. in diameter, containing paraffin of high boiling point to serve as a heating or cooling bath, and provided also with a thermometer. In plotting a heating or cooling curve, the paraffin bath was adjusted by hand to a temperature a few degrees above or below the transition point. The "mush" in the inner tube was stirred at intervals of thirty seconds to two minutes, according to the velocity of heating or cooling, and the thermometer was read immediately after.

The arrest-temperatures observed in this way during heating and cooling, together with the conditions under which the heating and cooling were carried out, are shown in table II.

TABLE II.

Arrest-temperatures of Ammonium Nitrate suspended in a bath of Liquid.

	Arrest-points (corrected).	Temperature of outer bath.	Composition of liquid.
Heating :	125.21	130°	Nitrobenzene.
	125.16	140	Xylene and ethylene bromide.
	125.38	140	Xylene and ethylene bromide.
	125.22	130	Xylene and tribromoethane.
	125.25	130	Nitrobenzene.
Mean	125.24°		
Cooling :	125.27°	120°	Xylene and ethylene bromide.
	125.21	120	Xylene and ethylene bromide.
	125.09	120	Xylene and tribromoethane.
Mean	125.19°		

These values may be compared with those given by Vogt (*Physikal. Zeitsch.*, 1911, **12**, 1129), who obtained with a dilatometer the upper and lower limits 125.25° and 125.13°, mean 125.2°. The eight values now recorded range from 125.09° to 125.38°. The mean of the five readings obtained by heating the salt is 125.24°, whilst the mean of the three readings obtained by cooling is 125.19°. The general mean of all the readings is 125.22°, and this is probably the best value for the transition-temperature. In view, however, of the difficulty of reading the temperatures to 0.01°, we prefer to give the transition-temperature to a tenth of a degree at 125.2°.

III. Transition-temperature at 84.2°.

The transition at 84° is accomplished by an abrupt expansion which frequently made itself manifest by fracturing the glass vessel in which a cast sample of nitrate was being cooled. There is, however, a very strong tendency for over-cooling to occur, and in many cases the salt was cooled to 32° without any indication that this change of crystalline form had taken place. In order to ensure the conversion of the δ - into the γ -form, it was necessary to inoculate the surface of the block with particles of the salt which had been heated to 60°, and to assist the conversion by scratching the surface with a sharply pointed glass rod. Even under these conditions, the over-cooling was usually very pronounced; the change of crystalline state (even in the vacuum-jacketed apparatus used successfully to record the change of state at 125°) only began when the temperature had fallen to 82° or below, and the latent heat was then not sufficient to restore the temperature to the transition point or to produce a horizontal arrest in the cooling curve. In

every case, therefore, the transition merely produced a sinuous curve, the highest temperature recorded for the maximum on this curve being 82.7° .

The first well-marked arrest of temperature at the transition point was observed when heating a sample of the powdered salt in a machine in which the nitrate was thrown over and over in such a way that the bulb of a thermometer was constantly bathed in the falling nitrate. A small machine in which this principle was embodied gave well-defined arrests on heating at 84.3° , 84.2° , 84.3° , and 83.3° , the first three values being concordant within one-tenth of a degree. It is remarkable that this transition-temperature, which was found to be so exceptionally difficult to locate by the methods first employed, proved to be by far the easiest of the transition points to determine exactly when once the proper conditions were established.

The most favourable conditions for determining this transition point were those already described in connexion with the change of state at 125.2° , namely, to compensate for the lack of thermal conductivity by stirring the powdered salt in a bath of liquid of almost equal density. The liquid used for this series of experiments was a mixture of ethylene bromide (D 2.18 ; b. p. 131°) and xylene (D 0.86 ; b. p. 140°). Special precautions were again needed to prevent "lag" in the change of state; the "mush" was therefore inoculated during heating with crystals heated to 100° , and during cooling with crystals heated to 60° . The inoculation was carried out just before reaching the transition point, and was followed by gentle stirring. The arrest points recorded in this way, which are lower than the mean of Zawidzki's arrests at 85.4° , but higher than the dilatometric readings 82.16° to 82.36° of Vogt, are set out in the following table:

TABLE III.
Arrest-temperatures of Ammonium Nitrate suspended in a Bath of Liquid.

Arrest-points (corrected).	Temperature of outer bath.	Composition of liquid.
Heating: 84.20°	90°	Xylene and ethylene bromide.
84.16	90	" "
84.25	90	" "
84.20	90	" "
Mean 84.20°		
Cooling: 84.28°	Falling slowly.	Xylene and ethylene bromide.
84.13	" "	" "
84.18	" "	" "
Mean 84.20°		

In this case, the means of the four values obtained during heating and of the three values obtained during cooling are identical. The transition point may therefore be fixed, probably within a few hundredths of a degree, at 84.20° , or may be given to a tenth of a degree as 84.2° .

IV. Transition-temperature at 32.1° .

(a) *Heating and Cooling Curves.*—The transition-temperature in the neighbourhood of 32° is more easily observed than either of those occurring at a higher temperature, since a prolonged arrest in the neighbourhood of 32° can always be detected when the nitrate is cooled through this temperature; indeed, both this arrest and that at 84° are constantly encountered when the nitrate is handled commercially. In spite of this fact, exceptional difficulty is experienced in securing an exact determination of this transition-temperature. This difficulty was ultimately traced to the fact that over a range of about a quarter of a degree on either side of the true transition point, the velocity of change of state is so slight as to be practically imperceptible, with the result that the conversion usually takes place at a temperature definitely below the transition point on cooling and at a temperature definitely above it on heating.

Large numbers of cooling curves were plotted in order to determine this transition-temperature accurately. In some experiments only a sinuous cooling curve was obtained, but in others well-marked horizontal arrests were recorded at the following temperatures:

Cast blocks	$31.9^\circ, 32.0^\circ, 32.0^\circ$.
Pressed blocks	$31.7^\circ, 31.5^\circ, 31.4^\circ, 31.8^\circ$.
Loose crystals	31.6° .

Horizontal arrests were also recorded, sometimes at lower temperatures, for example, $31.0^\circ, 29.5^\circ, 29.6^\circ$.

Arrests during heating were always at a higher temperature, and the curves were generally of a sinuous form, rising to a maximum value before falling again to a minimum approximating to the transition-temperature of the salt. These minima in the heating curves were observed at the following temperatures:

Cast blocks	33.2° .
Pressed blocks	$33.8^\circ, 33.1^\circ, 33.2^\circ$.

In one experiment in which the sample had become very much over-heated before the change of state set in, a still higher reading was obtained at 35.3° (compare Zawidzki, *loc. cit.*, who obtained

an average of 35.0° for seven arrests in heating ammonium nitrate alone and mixed with silver nitrate).

In view of the fact that the horizontal arrests or maxima in the cooling curves were always very much more fully developed than the minima in the heating curves, it was believed that the former could be assumed to give a correct value for the transition-temperature which was located provisionally at 32° ; actually, however, the data now quoted can only be used to prove that the transition-temperature lies within certain limits, for example, between 32.0° and 33.1° , and it was not possible to secure an absolute determination by this method in view of the fact that in no case were the arrests on heating and cooling within one degree of each other.

Attempts to secure more accurate readings of these transition-temperatures by using larger quantities of nitrate up to a kilogram resulted in failure, the conductivity of the salt being so low as to prevent the effective flow of heat from one part of the mass to another; better results were, indeed, always obtained by heating or cooling much smaller quantities of ammonium nitrate, insulated as carefully as possible, for example, in a vacuum vessel, in order to reduce the rate of heating or cooling to a minimum. A distinct improvement in the heating curves was, however, obtained, as in the case of the transition at 84° , by stirring about 700 grams of powdered nitrate in a small drum, surrounded by a steam-jacket, in such a way as to produce a constant flow of nitrate past the thermometer. By using this method, the following arrests in the heating curves were recorded:

32.6° , 32.75° , 32.7° , 32.9° , 33.0° .

These readings are definitely lower than those recorded previously when cast or pressed blocks of the nitrate were heated, but no improvement could be effected in the cooling curves, so that there still remained a gap of about 0.6° between the highest arrest on cooling and the lowest arrest on heating.

The method of stirring the powdered nitrate in a bath of liquid of equal density, which had proved so successful at the higher temperatures, was a complete failure when applied to the determination of the transition-temperature at 32° . The temperature recorded on the thermometer immersed in the liquid frequently failed to show any arrest at all. Even after inoculation, the cooling curves were extremely erratic, and only on two occasions were satisfactory arrests observed at 31.8° and at 31.6° ; on no occasion was an arrest observed in the heating curve. It may be noted, however, that Müller (*Zeitsch. physikal. Chem.*, 1899, **31**, 354) obtained a satisfactory arrest at 32.2° by cooling from 80° a mix-

ture of 100 grams of ammonium nitrate with 15 to 20 grams of water, and that this temperature lies within 0.1° of our final value for this transition point.

(b) *Experiments with the Dilatometer.*—The unexpected difficulties which were encountered in trying to determine the exact position of the transition-temperature at 32.1° can be traced to the relative slowness with which the change of state takes place immediately above or below the transition point, even when assisted by inoculation, as contrasted with the much greater velocity of the changes at 84° and 125° .

This is in accordance with the general rule that changes of this character become more and more sluggish as the temperature falls, by reason of the decreasing mobility of the molecules and the increasing resistance which the rigidity of the material opposes to molecular rearrangement. Under such conditions, the thermal method becomes difficult or impossible, and it is usually necessary to fall back on some method of determining the transition-temperature in which ample time can be allowed for the change of state to reveal itself. In the case of ammonium nitrate, the most promising method was to follow, by means of a dilatometer,* the expansion or contraction which accompanies the change of state, instead of relying on the absorption or liberation of latent heat to produce an arrest in the heating or cooling of the salt.

Experiments which were made on these lines gave us our first trustworthy value for this transition-temperature, and also provided valuable information as to the velocity of the change in the immediate neighbourhood of this point.

The solid used in the dilatometer was made by fusing pure, dry ammonium nitrate, pouring into a mortar, breaking the cast lump into pieces about 0.3 cm. in diameter, and sieving to free it from dust. This form of the salt was used in order to secure good thermal contact between the solid and liquid, and, at the same time, to avoid the risk of fracturing the bulb by the sudden expansion of a closely-packed powder. The dilatometer held about 60 c.c., and the bulb was sealed off after filling about three-quarters full with fragments of nitrate. The liquid was a paraffin of high boiling point which had been treated with concentrated sulphuric acid to free it from olefines, and then dried over metallic sodium; it was introduced in an air-free condition by making use of the apparatus shown in Fig. 1 of a paper by Wade and Merriman (T., 1912, 101, 2430).

In a dilatometer filled in this way, there are at the transition-

* Compare van't Hoff, *Zeitach. physikal. Chem.*, 1895, 17, 130, and "Vorlesungen," 1898, vol. i., p. 18.

temperature two alternative positions for the meniscus; one, which may be called $V\beta$, is the position when all the nitrate is still in the stable low temperature or β -form; the second, which may be called $V\gamma$, is the position to which the meniscus rises when all the nitrate has been converted (without change of temperature) into the lighter γ -form. The position $V\beta$ can be determined by heating the dilatometer from the atmospheric temperature to a point just below the transition point; $V\gamma$ can be determined by heating the dilatometer, say to 50° , until the whole of the nitrate has passed into the γ -form, and then cooling it to a point immediately above the transition point at 32° ; very little extrapolation is then required to give the exact position of these two points.

In using this method to determine the transition-temperature of ammonium nitrate, it is essential that the dilatometer should contain both forms of the salt, in order that change of state may take place quite readily in either direction. This condition was secured by heating the dilatometer to 50° , when the meniscus rose to a point well above $V\gamma$; on immersing the dilatometer in cold water, part of the salt reverted from the γ - to the β -form, a change which was revealed at once by the appearance of white patches on the lumps of nitrate; this change took place long before the contents of the bulb as a whole had time to cool to the transition-temperature. Having made sure in this way that the nitrate in the bulb contained a substantial proportion both of the β - and of the γ -forms of the salt, it was possible to find a range of temperatures (just above the transition point) at which the meniscus tended to settle down in the neighbourhood of $V\gamma$ by reason of the complete conversion of the contents to the γ -form, and a range of temperatures (just below the transition point) at which the meniscus would settle down in the neighbourhood of $V\beta$, owing to the complete conversion of the nitrate to the β -form.

The actual behaviour of the dilatometer when heated at different temperatures after the preliminary treatment described in the preceding paragraph was as follows:

(i) When the dilatometer was immersed in a thermostat at 32.2° , the meniscus settled down very quickly to a definite position between $V\beta$ and $V\gamma$, and during the course of two hours showed no tendency to rise to $V\gamma$ or to fall towards $V\beta$. The change of state appeared, in fact, to be arrested at the point to which it had been brought by the more drastic preliminary treatment of the salt. A precisely similar behaviour was observed at 32.1° , 32.0° , 31.9° , 31.8° , and 31.7° .

(ii) When the temperature of the thermostat was reduced to 31.6° , the meniscus for the first time began to show a tendency to

fall towards $V\beta$, although the change at this temperature was so slow as to be almost imperceptible; on repeating the experiment with the thermostat set to 31.5° , however, a definite movement towards $V\beta$ could be seen. These two temperatures are therefore definitely below the transition point of the nitrate.

(iii) When, on the other hand, the temperature of the thermostat was raised to 32.3° , a definite but exceedingly slow upward movement of the meniscus towards $V\gamma$ was observed, and a more pronounced movement when the temperature was raised to 32.7° .

These experiments, on account of the extreme sluggishness of the change of state in the immediate neighbourhood of the transition point, failed to fix the exact position of this temperature, although they served to locate it between 31.6° and 32.3° . These two limits agree quite closely with those arrived at from a study of the cooling and heating curves, which had shown arrests below and above two corresponding limits at 32.0° and 32.6° ; rather closer limits were recorded by Vogt, who observed equal and opposite slow changes of volume at 32.40° and 32.62° .

(c) *Quantitative Experiments with the Dilatometer.*—In order to determine the exact position of the transition point, a series of quantitative experiments was made on the velocity of the change of state as shown by observations with the dilatometer at temperatures above and below the transition-temperature.

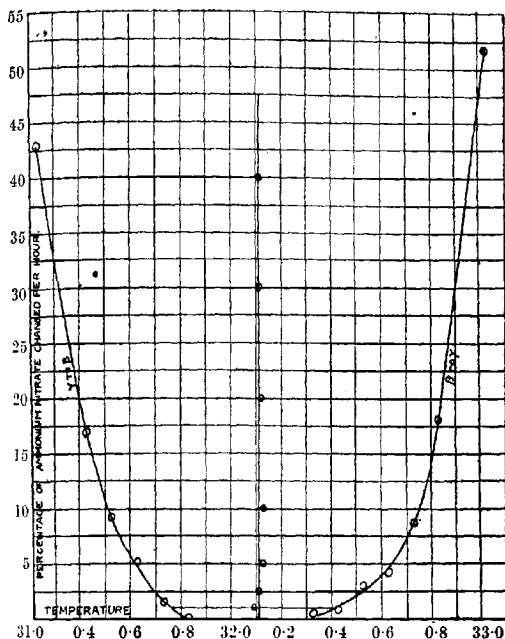
The preliminary treatment of the nitrate was much the same as in the previous experiments, and was carried out as follows. The two extreme positions of the meniscus at the transition-temperature were first located on the scale of the dilatometer, as follows:

$$V\beta = 20 \text{ cm.}; V\gamma = 48 \text{ cm.}$$

Starting with cold nitrate in the β -form, the dilatometer was next immersed in a bath of water at 34° in order to initiate the change from the β - to the γ -form. At this temperature (on account of thermal expansion), the two extreme positions of the meniscus would be about 22 and 50 cm.; when, therefore, the meniscus had risen to about 36 cm. on the scale of the dilatometer, it was clear that the two forms were present in roughly equal quantities, whilst the thermal conditions of the dilatometer and its contents had not been seriously disturbed.

After this preliminary treatment, the dilatometer was immersed in a thermostat set to a definite temperature just above or below the transition point. Thermal equilibrium was quickly established, and exact measurements could be made of the rate of movement of the meniscus consequent on the change of state from

β to γ , or vice versa; the uniformity of this movement, over considerable periods of time, was such as to justify the view that the rates recorded in heavy type in table IV are definite physical constants of the change of state over the range of temperatures from 31.2° to 33.0° . The readings represent the movement in mm. of the meniscus during successive intervals of ten minutes. The mean steady velocities (obtained by averaging the numbers which are shown in heavy type in table IV) are recorded in similar units.



The final column shows the percentage of the salt which would undergo change of state in one hour, as deduced from the volume changes recorded in the previous columns. The thermometer readings are given to tenths of a degree, but are all subject to a correction of $+0.03^\circ$. It is remarkable that at temperatures a whole degree above or below the transition point, nearly an hour is required to change half of the material from the β - to the γ -form, or vice versa.

When all these velocities are plotted out in a diagram, as in

the figure, a curve is obtained which is almost symmetrical on either side. According to the well-known principle which is used in determining the "critical volume" of liquids and vapours, the transition-temperature may be determined accurately by ruling a series of horizontal lines across the velocity diagram, reading off the temperatures given by the intercepts of these lines with the curve, and working out an average value for each pair of temperatures. These averages, as set out in table V below, are as follows:

32.09°, 32.11°, 32.13°, 32.13°, 32.12°, 32.11°, 32.11°.

The mean value, 32.11°, is much more accurate than any of the values deduced either from arrests in the heating and cooling curves of the salt or from merely qualitative observations with the dilatometer, and is probably correct to within a few hundredths of a degree. For practical use, the second decimal may be omitted, and the transition-temperature given to one-tenth of a degree as 32.1°.

(d) *Form of Velocity Curve.**—Whilst the use of the dilatometer in determining transition-temperatures has been a well-known standard method for more than twenty years, and has been applied repeatedly when the change of state is too slow to be followed by the thermal method (see especially E. Cohen's experiments on the allotropy of metals); the complete velocity curve shown in the figure does not appear to have been plotted in any of these cases. The most striking feature of this curve is its complete symmetry, as proved by the constancy of the temperatures shown in the last column of table V, which only vary over a range of $\pm 0.02^\circ$. This complete symmetry, which could not be predicted, makes it possible to locate the transition temperature very accurately, and it is doubtful if any other method is capable of giving equally exact results; for comparison, it may be noted that the use of the "rectilinear diameter" to determine critical volumes depends on the existence of a skew-symmetry only in the curve of specific volumes for the liquid and saturated vapour.

In view of the regularity of the curve it is of interest to inquire into its mathematical form. The data now recorded can be expressed by the equation

$$\pm(t - t_0) = \log_{10}(\sqrt{v} + 1),$$

where t = temperature,

t_0 = transition temperature,

v = velocity of change (percentage changed per hour).

* Added 6/12/19.

The agreement of this formula with the experimental results is shown in the following table:

<i>v.</i>	$\pm(t-t_0)$	$\pm(t-t_0)$
	obs.	calc.
1	0.33°	0.30°
2.5	0.41	0.41
5	0.50	0.51
10	0.62	0.62
20	0.72	0.74
30	0.79	0.81
40	0.86	0.86

(e) *Anomalies in the Heating and Cooling Curves.*—At a very early period in the investigation, it was noticed with some surprise that very steady arrests of heating and cooling might occur at temperatures which were obviously not exact transition points, since they were scattered over a considerable range on either side of a mean value, which could be regarded provisionally as the correct transition-temperature. This was an anomaly for which no explanation could be suggested at the time.

General experience in such matters has shown that when dealing with rapid transitions, such as are observed in iron at 895° and 766°, the arrest in the cooling curve becomes blurred whenever liberation of latent heat fails to compensate for loss of heat by cooling; a lowered arrest point is therefore nearly always revealed by its sinuous character. In dealing with ammonium nitrate, many sinuous arrests have been observed at temperatures either below or above the real transition point, but in several cases the arrests recorded at these lower or higher temperatures were perfectly sharp.

These observations can all be interpreted in the light of the data now given for the velocity of change of state. Thus, in the first place, it is obvious that since this velocity of change is imperceptible from 31.8° to 32.3°, there can be no marked liberation or absorption of latent heat and no arrest in the cooling or heating between these limits. Outside these limits of temperature, the flow of latent heat may arrest the cooling or heating, but the conditions are such that the arrest point cannot be regarded as a fixed temperature, but must be considered as a variable temperature depending directly on the rate of heating or cooling. Thus, taking the latent heat of the transition as 5.02 calories per gram, and the velocities of change of state as recorded in table IV, the temperatures of arrest for the different rates of cooling and heating shown in column 2 of table V are given in columns 3 and 4 of that table.

TABLE IV.
Velocity of Change of State, above and below 32.1°.

Temperature.*	Motion of meniscus, in mm. per 10 minutes.												Mean rate in mm. per 10 minutes.	Percentage changed per hour.
	33.8	25.0	20.0	21.0	—	—	—	—	—	—	—	—	20.0	42.8
31.4	8.4	9.6	8.3	8.2	8.1	7.5	7.5	—	—	—	—	—	7.9	16.9
31.5	11.0	2.1	2.2	3.0	3.7	4.2	4.5	4.5	4.3	4.7	4.3	4.0	4.3	9.2
31.6	1.4	1.2	1.9	1.9	2.0	2.2	2.5	2.4	2.4	2.4	2.3	—	2.4	5.2
31.7	0.8	0.8	0.4	0.4	0.7	0.7	0.6	0.7	0.6	0.6	0.6	0.6	0.64	1.4
31.8	10.5	1.1	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
32.0	—	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
32.2	6.5	0.5	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
32.3	7.0	1.2	0.3	0.7	0.3	0.2	0.3	0.2	0.2	0.2	0.2	0.3	0.23	0.5
32.4	—	1.7	1.6	0.1	0.4	0.2	0.2	0.3	—	—	—	—	0.30	0.7
32.5	13.7	4.7	3.0	2.3	2.2	1.7	1.5	1.5	1.4	1.4	1.2	1.2	1.4	3.0
32.6	4.8	7.6	3.5	2.3	2.8	2.5	2.0	1.7	1.9	1.7	1.6	—	1.9	4.1
32.7	9.0	7.9	7.0	5.7	5.0	4.8	4.0	4.0	4.0	4.0	—	—	4.0	8.6
32.8	18.4	18.0	17.7	17.2	17.2	17.2	16.8	16.8	16.4	16.3	16.6	16.6	8.4	18.0
33.0	21.7	22.9	23.8	24.3	24.4	24.1	—	—	—	—	—	—	24.1	51.7

* Correction at each temperature $\pm 0.03^\circ$.

† 8 minute intervals.

TABLE V.

Velocity of Change of State of Ammonium Nitrate at Different Temperatures.

Per cent. changed per hour.	Rate of cooling or heating. Calories per gram per hour.	Temperature (arrest-points).		Average temperature.
		Cooling.	Heating.	
1	0.050	31.75°	32.42°	32.09°
2.5	0.126	31.69	32.52	32.11
5	0.251	31.63	32.63	32.13
10	0.502	31.51	32.75	32.13
20	1.00	31.40	32.84	32.12
30	1.51	31.32	32.90	32.11
40	2.01	31.25	32.96	32.11
Mean				32.11°

The arrest points shown in the table are the temperatures at which the latent heat, liberated by a change of state proceeding with known velocity, would exactly balance the heat gained or lost by radiation, conduction, etc. Imperfect conduction of heat in the mass may displace these temperatures still further from the true transition point, and at the same time destroy the sharpness of the arrests. The latter phenomenon is observed also in the transitions at 84° and at 125°, where sinuous arrests at abnormally low temperatures are frequently observed, but the velocity of change of state at these two points is so much greater that a prolonged or "horizontal" arrest has never been observed, except at a temperature agreeing very closely with one or other of these transition points.

Summary.

(1) The freezing point of ammonium nitrate is very sensitive to the influence of traces of moisture; by careful purification and drying it has been raised to 169.6°.

(2) The highest of the transition points has been determined from the arrests of temperature on heating and cooling the salt when suspended in a liquid of similar density. The temperatures recorded were: on heating, 125.24°; on cooling, 125.19°; mean value, 125.2°.

(3) The second transition point was determined by the same method, the observed temperatures being: on heating, 84.20°; on cooling, 84.20°; mean value, 84.2°.

(4) The lower transition point cannot be determined in this way, as the change of state is too slow to be detected over the range from 31.8° to 32.2°. It was determined dilatometrically by measuring the rate of change over a range of temperatures; the

curve of velocities proved to be symmetrical, and the transition-temperature was therefore found by taking the average of pairs of temperatures at which the change proceeded with equal velocities in opposite directions. In this way, the transition-temperature was fixed at 32.1° .

(5) The form of the velocity curve for the change of state can be expressed by the simple empirical equation

$$\pm(t - t_0) = k \log_{10} (\sqrt{v} + 1).$$

(6) The arrest points due to the change of state at 32.1° never coincide with this temperature, the arrest point being determined by the rate of loss or gain of heat. A table is given showing the temperatures of arrest on cooling or heating at fixed rates expressed in calories per gram per hour.

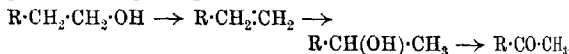
GUY'S HOSPITAL,
LONDON, S.E. 1.

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CXXXII.—*The Production of Methyl Ethyl Ketone from n-Butyl Alcohol.*

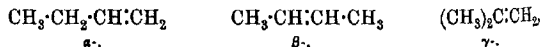
By ALBERT THEODORE KING.

IN this conversion, the usual series of steps has been employed of dehydration, re-hydration of the resulting alkylene to the secondary alcohol, and, finally, dehydrogenation of the latter to give the corresponding ketone:



No details appear to have been published hitherto regarding the hydration of butylene to the secondary alcohol, and although the first and last of the above stages have in this particular case been elsewhere described, the comparative results now obtained seem worthy of being placed on record also.

Dehydration of n-Butyl Alcohol.—Each of the three possible butylenes,

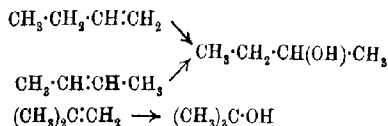


has been identified by previous observers in the product of dehydration, the composition of which would appear to depend both on the nature of the dehydrator and on the temperature employed. Thus Ipatiev (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 577), with

lumina as catalyst, at 500° obtained a gas containing 25–30 per cent. of α -butylene, the rest being γ -butylene; the latter was attributed to the presence of isobutyl alcohol in the material employed. Senderens (*Ann. Chim. Phys.*, 1912, [viii], 25, 449), using aluminium sulphate at 300°, obtained α -butylene with 27 per cent. of γ -butylene. Le Bel and Green obtained on dehydration with zinc chloride a product free from γ -butylene and containing 30 per cent. of β -butylene and 10 per cent. of α -butylene (*Bull. Soc. chim.*, 1881, [ii], 35, 438).

In the present investigation, in which phosphoric acid on pumice was used, only slight differences were observed in the composition of the product at temperatures ranging from 280° to 400°. No γ -butylene was detected, and even at 280° the amount of α -butylene present, so far as was indicated by fractionation of the bromide, could only be slight. This method of dehydration, therefore, yielding reasonably pure β -butylene, gives a much more homogeneous product than those previously described.

Hydration of Butylenes.—The hydration of the three butylenes with sulphuric acid should theoretically proceed as formulated below:



This conversion in the case of γ -butylene has been described by Butlerov (*Annalen*, 1875, 180, 245), who also records the very slow hydration of β -butylene, but without details of the isolation of *sec.*-butyl alcohol. Nor is the formation of the latter from α -butylene recorded; and this point is under examination, the present investigation dealing only with the behaviour of β -butylene.

The rapid absorption of β -butylene (as also of α - and γ -butylene) by concentrated sulphuric acid is well known, but by this action polymerisation, and not hydration, results. With diluted acid, the very slow action on keeping has been confirmed, but liquefied β -butylene, under its own pressure, agitated in contact with the acid, has been found to undergo absorption with ease. Polymerisation, which is marked at the higher concentrations, is very slight with 78 per cent. acid, and below this strength the reaction proceeds normally.

In one case, an absorption was observed of nearly 20 per cent. in excess of the butylene theoretically required to convert the acid to butylsulphuric acid, suggesting that the latter is capable of

catalysing the direct hydration of β -butylene. It is hoped to investigate this point further.

The diluted solution, on distillation, readily gives the secondary alcohol in good yield.

Dehydrogenation of sec.-Butyl Alcohol.—Reduced copper is recorded by Sabatier and Senderens as being particularly efficient in catalysing the dehydrogenation of secondary alcohols, these showing a conversion without complications, but incomplete owing to the reverse action also taking place in the presence of copper. They observed the formation from *sec.*-butyl alcohol of methyl ethyl ketone and pure hydrogen, without any accessory reaction, within the temperature range of 160–300° (*Ann. Chim. Phys.*, 1905, [viii], 4, 433, 465). In the present work, the reverse action above referred to was perceptible, but only slight.

EXPERIMENTAL.

Preparation of β -Butylene.

The *n*-butyl alcohol distilled at 116–118°. It was gently boiled in a silica distilling flask attached to a 2.2 cm. copper tube 150 cm. in length, capable of giving, by electrical heating, temperatures, registered at the middle part, from 280° to 400°. This was packed with fragments of ignited pumice impregnated with glacial phosphoric acid. (This catalyst can be used indefinitely, its activity being renewed occasionally by burning a piece of phosphorus at the mouth of the tube, with a current of air passing through.) The unchanged alcohol and water formed were collected in a receiver with water-cooled reflux and with a syphon tube for the discharge of the condensate from time to time. The gaseous product, after scrubbing with 60 per cent. sulphuric acid to retain any γ -butylene, was absorbed in cooled bromine until the latter was nearly colourless. The product was then shaken with dilute alkali, dried with calcium chloride, and systematically fractionated. The following are typical results:

	(1).	(2).	(3).
Temperature	300–320°.	280–300°.	400°.
Dried product	75 grams.	114 grams.	120 grams.
<i>Final fractions:—</i>			
below 153°	(153–157° 7 grams)	3.5 "	2 "
155–157°	—	9.0 "	8 "
157–159	60 "	92 "	98 "
159–161	3 "	3 "	5 "
residue	3 "	3.5 "	4 "

The boiling points of the three dibromides are: α -, 166°; β -, *cis*-form, 158°; *trans*-, 161°; γ -, 149-6°. Thus α -butylene is not present, even at the lowest temperature employed, in notable quantity. The low fraction, possibly indicating the presence of γ -butylene, was not appreciably increased in (2), in which washing with 60 per cent. acid was omitted, and these lower fractions were not in sufficient quantity to detect by further fractionation the presence of γ -butylene dibromide. Moreover, no *tert*-butyl alcohol was obtained from the 60 per cent. acid used to wash more than 100 grams of gas. On dilution and distillation, it yielded only 3 grams of product, which proved to be mainly *n*-butyl alcohol carried over.

Much of the butylene formed dissolves in the butyl alcohol which escapes dehydration and condenses in the receiver. From this solution, more than 150 times its volume of butylene is expelled on raising to boiling point.

No side-reaction was observed in the dehydration. The unchanged alcohol layer, dried and fractionated, yielded, finally, 1-2 per cent. distilling below 116°, the rest passing over at 116-118°, and for continuous working the condensate was shaken with salt and the upper layer separated and used again, thus conserving the dissolved butylene.

Action of Sulphuric Acid on β -Butylene.

On bubbling the gas through concentrated sulphuric acid, rapid absorption took place, the liquid becoming warm and darkening in colour. A pale yellow upper layer formed, and when this had increased to about 10 c.c. in volume, it was separated, washed, and dried with calcium chloride. It had a slight odour of hydrocarbon, and, on distilling, boiled without any constancy from 140° to 300°. The sulphuric acid layer gave, on pouring into excess of water, a turbid liquid, from which a small quantity of oil separated, which gradually darkened and became very viscous. These products, presumably formed by polymerisation of the β -butylene, were not further investigated. No secondary alcohol was detected in the aqueous portion.

With diluted acid, even up to 78 per cent., no appreciable absorption took place when the gas was merely bubbled through. For absorption under pressure, the following procedure was used.

The gas was liquefied by passing through a worm cooled in a mixture of ice and salt, the outlet tube dipping under the acid contained in a stout-walled bottle, also cooled in ice and salt. This gave good condensation, bubbles of gas escaping only at rare

intervals. The bottle was then closed by a rubber stopper, wired down, and, after weighing to ascertain approximately the amount of butylene condensed, shaken in a mechanical shaker until the butylene layer had disappeared. In each case, 50 c.c. of pure acid were used with varying dilution, and the time occupied for absorption was roughly noted, with the following results:

Concentration. Per cent.	Butylene. Grams.	Time taken.
100	17	—
84.0	21	5 minutes
78.0	23	20 "
76.0	22	40 "
75.3	22	1 hour
72.5	19	1.6 hours
70.0	24	5 "
64.8	10	8 "
50.0	22	Little effect after 15 hours.

With pure acid, the absorption was complete in a few seconds. On pouring into ice, an oil separated which, after drying with calcium chloride, weighed 15 grams. It distilled from 140° to above 300° without boiling constantly at any point, like the product previously described. No secondary alcohol was present in the aqueous portion.

With 84 per cent. acid, the alcohol was the main product, but considerable polymerisation occurred. Moreover, the acid crystallised in the freezing mixture, causing inconvenience through blocking of the delivery tube. The freezing-point curve shows the range of concentration, having sufficiently low freezing point and also giving normal reaction in reasonable time, to be from 74.5 (f. p. -20°) to 78 per cent. (f. p. -20°). The concentration ultimately adopted was 75 per cent. With 78 per cent. acid, a trace of oil with a terpene-like odour was observable on dilution, this becoming imperceptible with the lower concentrations.

The rise of temperature was very marked with the higher concentrations. The pressures generated by the liquid butylene were approximately determined by a pressure gauge as follows:

12°	0.6 atm.
20	0.95 "
30	1.4 "
40	1.9 "

With 75 per cent. acid, the temperature did not reach 40°, and the operation is thus without risk.

To ascertain the extent of absorption, 76 per cent. acid, containing 92 grams of pure acid, was shaken with 63 grams of butylene (theoretical quantity=51.5) for fifteen hours. The excess of gas was allowed to escape, and any in physical solution removed by

METHYL ETHYL KETONE FROM N-BUTYL ALCOHOL. 1409

exhaustion, when 61 grams were found to have been chemically absorbed. About 90 per cent. of the theoretical quantity was, however, usually employed.

Hydrolysis of Butylsulphuric Acid.

Comparative experiments were made, using three portions of 50 grams from the same batch of butylsulphuric acid. These were respectively neutralised with sodium carbonate and treated with quantities of 50 and 25 grams of water. The liquids were distilled, and the distillates caught in graduated tubes and thoroughly shaken with salt solution and a slight excess of salt. The volumes of upper layer were 23 c.c., 23 c.c., and 22.5 c.c. respectively. With neutralisation as employed by Butlerov (*loc. cit.*), the alcohol distilled over very slowly with a large quantity of water. Distillation with the lesser quantity of water gave a distillate with only a small aqueous layer, the bulk being retained by the acid, but with a slightly lower yield, although no ether was detected in the product. Dilution with an equal weight of water was therefore adopted.

With this procedure, 51 grams of butylene yielded a distillate which, after salting out and drying with potassium carbonate, weighed 60 grams, that is, 89 per cent. of the theoretical on the crude material. From 150 grams of dried, undistilled product, after careful fractionation, were obtained as final fractions:

below 97.5°	3 grams
97.5—99.5°	131 "
99.5—100°	8 "
residue	5 "

The fraction 97.5—99.5° was employed for conversion to ketone.

Dehydrogenation of sec.-Butyl Alcohol.

The procedure followed was substantially that of Sabatier and Senderens (*loc. cit.*). A copper tube 172 cm. long and 1.2 cm. in diameter was packed with copper oxide from wire kept in place with plugs of rolled copper gauze, and enclosed in a 2.5 cm. copper tube 135 cm. long wired for electrical heating. After reduction of the wire with ethyl alcohol vapour, and expulsion of the latter, *sec.*-butyl alcohol was distilled through from a silica flask at such a rate that the distillate passed through at the rate of about one drop a second. This was caught in a receiver cooled in ice-water. The hydrogen was evolved just too fast to allow the bubbles through a wash-bottle to be counted. The temperature remained

1410 ARMSTRONG AND HILDITCH: CONVERSION OF THE SIMPLE

fairly constant throughout, the fluctuation on either side of 2900 being never more than 5°.

In the first preparation, from 100 grams of alcohol, 104 of distillate were obtained. This contained water, formed from some unreduced copper oxide, and, on fractionating, 94 grams distilled at 73—75°, the mixture separating a small, lower layer of water. After drying with potassium carbonate, the bulk distilled at 79—81°.

Two hundred and fifty grams of alcohol gave an almost theoretical yield of dried, undistilled product, which gave the following fractions:

76—79°	5 grams
79—81	199 "
81—82	9 "
82—86	6 "
residue	12 "

Thus the conversion is upwards of 90 per cent.

The fraction boiling at 79—81° decolorised permanganate, but after stirring with about half a gram of powdered potassium permanganate for a short time, the colour persisted. On distilling off and drying thoroughly with potassium carbonate (the boiling point is very easily affected by traces of water), the ketone distilled almost completely within the range 80—80.6°.

The yield on the small scale from the crude butylene is about 70 per cent. of the theoretical, and with continuous working and recoveries this figure at least should be reached in the complete synthesis from *n*-butyl alcohol.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.

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CXXXIII.—*Conversion of the Simple Sugars into their Enolic and Ethylene Oxide Forms.*

By EDWARD FRANKLAND ARMSTRONG and THOMAS PERCY
HILDITCH.

No group of compounds is more remarkable than that of the hexoses, on account of their extreme mutability. Glucose, for example, may be obtained in an α - and a β -crystalline form, and if either of these is dissolved in highly purified water the solution is all but stable. Yet if a trace of alkali is added, an equilibrated

mixture of the two isodynamic forms is practically instantaneously produced. The change has been specially studied by Lowry (T., 1903, **83**, 1314; 1904, **85**, 1551), and its character has been discussed also by one of the authors (T., 1903, **83**, 1305).

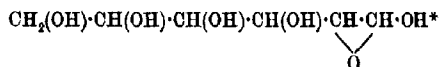
The more gradual change, also under the influence of alkali, from one hexose into another, within sections including as many as four members of the group (for example, glucose \rightleftharpoons mannose \rightleftharpoons fructose \rightleftharpoons glucose), was brought to light through the painstaking labours of the late Lobry de Bruyn (*Rec. trav. chim.*, 1895, **14**, 156, 204). In this case, the transition has been assumed to involve the formation of an enolic form as an intermediate term. In the case of the hexoses the aldehydic form (aldehydrol) is commonly supposed to have but an ephemeral existence, and it is held that α - and β -glucose are butylene oxide or pentaphane derivatives corresponding with the two methyl glucosides. The latter, it is well known, are simultaneously produced by the action of a strong acid on glucose dissolved in methyl alcohol; a residue, long unexplained, has recently been shown to contain a third isomeric methyl glucoside, regarded by Fischer and by Irvine as the derivatives of an ethylene oxide form of the hexose.

Irvine and his school (T., 1915, **107**, 524; 1916, **109**, 1305, etc.) have shown that the new methyl glucoside is characterised by its capacity to condense with acetone, to reduce potassium permanganate solutions, and to undergo auto-condensation, and that the activity of the parent glucose from which it is derived far exceeds that of α - or β -glucose.

The observations we have to place on record relate to the changes effected in the simple sugars by acids and by alkalis, as measured both by means of the polarimeter and by means of increased liability to oxidation.

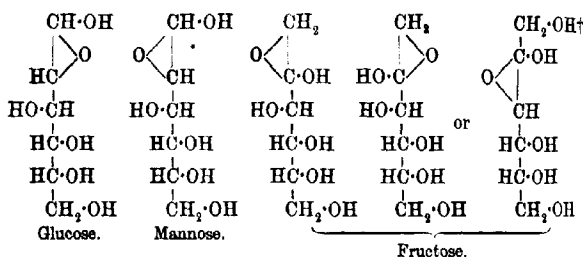
A solution of either α - or β -glucose in water (both well purified) is practically unaffected by permanganate. In acid solution, reduction of the permanganate sets in at once and at a definite rate under definite conditions; thus, under the standard conditions detailed in the experimental part, 10 c.c. of 1 per cent. of α - or β -glucose in *N*/10-hydrochloric acid solution decolorise 2 c.c. of *N*/100-permanganate solution at 25° in twenty-eight to thirty minutes. That the change is instantaneous is proved by the fact that the reducing power acquired is independent of the time during which the acid has acted, solutions containing acid which have been kept various times all having the same reducing power. The strength of the acid, however, is a factor in the change, the effect being less the weaker the acid and likewise the less concentrated the acid.

We consider that the active agent is the ethylene oxide modification of glucose,



The amount of the ethylene oxide form present is regulated by an equilibrium depending on the strength of the acid, but that it is small is shown by the fact that the optical rotatory power of glucose in an acid is the same as in an aqueous solution. The ethylene oxide form is reproduced as oxidation by the permanganate proceeds, as shown by the fact that fresh additions of permanganate solution are decolorised.

Mannose and fructose are affected by acids in a similar way, but the altered mannose solution acts far more rapidly than that of glucose; fructose is only slightly less active than mannose. For example, under precisely comparable conditions, whereas the reduction of permanganate by glucose occurs in twenty-eight to thirty minutes, that by mannose takes only from twelve to thirteen, and that by fructose sixteen to seventeen minutes.



In view of the close relation of the ethylene oxide forms of these sugars, it seems not improbable that one of the isodynamic forms is the more oxidisable, and that this is the form present in mannose.

The reduction of permanganate (as well as of methylene-blue and of indigo-blue) is also promoted by the addition of alkali. In

* At first sight the alterations involved in the conversion of butylene oxide into ethylene oxide or enolic forms of glucose appear somewhat far reaching when viewed only in the light of the conventional structural formulae. If, however, structural models are prepared of the sugars on the lines of the Pope-Barlow hypothesis of close packing a more rational interpretation of the changes is realised.

† This form of fructose is present in sucrose according to Haworth and Law (T., 1916, 109, 1314).

this case, however, the change of the hexose is more gradual, as, within limits, the solution is the more active the longer the alkali has acted. The interactions in the three cases take place at corresponding rates, showing that in each case the same change is being studied. Under the experimental conditions observed, the reduction phenomena correspond only with the changes in structure which take place in the course of the first few hours, and it is unlikely that any far-reaching disturbance has occurred in the carbon chain beyond the atoms 1 and 2.

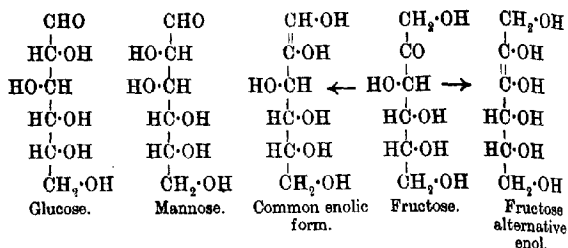
As shown by the polarimeter, the equilibrium between the α - and β -butylene oxide forms of the sugar is established instantaneously in alkaline solution, and subsequently the optical activity falls slowly, but it is still of considerable magnitude at the end of six hours. After this, it continues to fall, some fifteen to twenty days being required before the solution loses its activity. To judge from the slowness with which alkali acts as compared with acid, taking into account the instantaneous equilibrium of the α - and β -forms in the presence of alkali, it is clear that the latter are not concerned in the change. It therefore seems probable, so far as the effect produced by acids is concerned, especially in view of the distinctly basic character of ethylene oxide, that the ethylenic oxide form of the hexose, not an enol, is the active agent. Assuming the enol to be concerned, acids equally with alkalis should convert one hexose into another in the Lobry de Bruyn change, but this is known not to be the case.

It is noteworthy, however, that ethylene oxide itself has no reducing power on either methylene-blue or indigo-blue in alkaline solution, although it readily affects permanganate. It is by no means clear, in fact, that the action of alkali is comparable with that of acid, and it may well be that reduction is effected by the enol. Whereas possibly in acid solution a salt of the basic ethylene oxide hexose is formed, in alkaline solution the scission of all ring systems and the production of a metallic salt of the open-chain enol appears more probable.

Whilst glucose decolorised the standard amount of permanganate initially in eleven minutes (in the presence of one equivalent of sodium hydroxide), fructose takes three and mannose twenty-five minutes; the figures after the solutions have remained for five hours are, respectively, glucose 3, fructose 1.25, and mannose 9 minutes.

As the formulæ show, all three substances can give the same enolic form. On the supposition that "enol" rather than "ethylene oxide" is initially formed in the presence of alkali, the configuration represented by fructose is most, and that represented

by mannose least, prone to undergo enolisation. This is in marked contrast to the behaviour of the same three sugars towards acid.



The change in presence of alkali is qualitatively proportionate to the strength of the alkali. It is of special interest in this connexion that pyridine has a similar effect to the other alkalis. In this case, as pyridine is such a weak alkali, the sugars were dissolved in the base itself. Decolorisation of glucose took place initially in about fifty to sixty minutes, increasing to thirty minutes in about five hours, whereas with fructose the times were thirty minutes initially and eight minutes after six hours.

This observation is quite in harmony with the important part which pyridine and quinoline have played in sugar chemistry as the media in which epimeric changes are effected, causing the rearrangement of the groups attached to the asymmetric carbon atom at the end of the chain. Both in the interconversion of epimeric hexonic acids (E. Fischer, *Ber.*, 1890, **23**, 2625) and of epimeric glucosides (E. Fischer and von Mechel, *Ber.*, 1916, **49**, 2813; 1917, **50**, 711), formation of intermediate modifications must be involved.

The alterations in structure which we have followed by the changes in reducing power are clearly in no way related to those known as mutarotation. Whereas the former take place instantaneously in the presence of acid, and more slowly in the presence of alkali, mutarotation is brought about immediately in the presence of alkali and more slowly in the presence of acid.

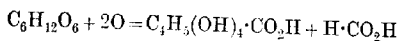
EXPERIMENTAL.

Reducing tests were made by withdrawing 10 c.c. of the sugar solution (generally 1 per cent., or 1/18 gram-molecule of hexose per litre, except when polarimetric comparisons were also made, in which case 5 per cent. solutions were used) into a stoppered test-tube and adding 2 c.c. of the standard permanganate or dye solution; *N*/100-potassium permanganate was invariably used, whilst

the dye solutions consisted respectively of a 0.025 per cent. solution of methylene-blue and a solution of neutral indigo sulphonates which contained 0.045 per cent. of indigotin. In those cases in which it was desired simultaneously to neutralise the acid or alkali present, special solutions of *N*/100-permanganate were employed containing respectively the amount of sodium hydroxide or of sulphuric acid per 2 c.c. necessary to neutralise the acid or alkali present in the 10 c.c. of sugar solution exactly.

The behaviour of permanganate with the sugar solutions varies considerably according to the conditions studied; thus, acid fructose or mannose solutions pass simply from pink to clear white, and perfectly definite end-points are obtainable in these cases. In other cases, generally those of slowly reducing acid media or of rapidly reducing neutral or alkaline solutions, the pink tint gives place, with varying rapidity, to a very pale yellow, and ultimately to the colourless, condition. A definite colour standard, just short of colourless, was adopted here, and sharp end-points could be obtained without difficulty. With slowly reducing neutral or weakly alkaline solutions, however, a precipitate of manganese dioxide of variable degree of fineness is apt to appear, and it is difficult to determine the precise point at which actual precipitation sets in; cases of this kind are denoted in the tables which follow by the addition of "indefinite" or "with pptn."

It is obvious that in the latter case the amount of reduction will not be so great as when the formation of the colourless manganous salt solution has occurred. In point of fact, whilst the 10 c.c. of sugar solution employed has contained 0.1 gram (1 per cent. solution) or 0.5 gram (5 per cent. solution) of hexose, the 2 c.c. of *N*/100-permanganate, assuming the action



to occur, are capable of oxidising 0.0009 gram of hexose if the reduction proceeds to the manganous state, or 0.00054 gram if the action is arrested at the stage of manganese dioxide.

In the extreme cases, therefore, we have measured the time of oxidation of 0.9 per cent. of the sugar present in the solution, whilst, on the other hand, we have dealt with the time of oxidation of as small a proportion as 0.11 per cent. or less of the sugar present.

The stock solutions of sugars, and also the portions undergoing tests, were maintained at 25° throughout.

Neutral Solutions.

The dye reagents are unaffected by any of the sugars tested in neutral solution. Under the conditions described, permanganate is decolorised by fructose in four or five hours, whilst with either form of glucose the solution becomes orange in about six hours, and fades to a full yellow tint after twenty-four hours. The behaviour of mannose is very similar to that of glucose. These results are obtained equally with fresh solutions and those which have remained for a day at 25°.

It may be of interest to state that if the test is conducted in *N*/10-sodium chloride solution instead of in water, precipitation of manganese dioxide sets in at a much shorter time; the figures obtained for fructose, α -glucose, and mannose were respectively 93, 90, and 115 minutes.

Acid Solutions.

(i) *Aqueous Solutions.*—The oxidation times are constant at any age of the solution in the case of acids. This is illustrated by the figures for fructose, α - and β -glucose, and mannose given in table I.

The dependence of the time factor on the hydron concentration is shown by the results in table II, wherein only the mean figures are quoted; it may be emphasised that the agreement of the individual readings at varying ages of the sugar solutions is in all cases as good as those given *in extenso* in table I.

Two series of times are given for each sugar, the first being for the simple acid solution; the second gives the values obtained when the test-solutions were neutralised simultaneously with the addition of permanganate.

In the case of the higher concentrations of hydrogen ions investigated, neutralisation of the acid present, effected at the same time as the addition of permanganate, does not appreciably alter the oxidation times.

At the lower concentrations of hydrogen ions, and notably with the weaker acids, such as phosphoric and acetic, the oxidation times for the "neutralised" solutions are quicker than for the acid solutions, and progressively so as the strength of the acid decreases.

The identity of the oxidation times for "neutralised" and for acid solutions with the stronger acid solutions is quite definite, and we consider that they indicate the persistence of the active form of the sugar after neutralisation of the acid has taken place; the meaning of the results with neutralised solutions of weaker acids is by no means clear, although they are explicable to a certain

extent when it is borne in mind that the sodium salts of the weaker acids will be appreciably hydrolysed, so that we have really passed over in this instance to a feebly alkaline solution of the sugar.

The age of the solution is given in hours, the first reading (0.1 hour) having been taken immediately solution was complete; in most instances, this reading was commenced about three to five minutes after the addition of acid. The times of oxidation are in minutes, unless an explicit statement to the contrary is added.

TABLE I.

One per cent. Sugars in $N/10\text{-HCl}$ and $N/10\text{-H}_2\text{SO}_4$.

Age.	Fructose.		α -Glucose.		β -Glucose.		Mannose.		Acid.
	Acid.	Neutd.	Acid.	Neutd.	Acid.	Neutd.	Acid.	Neutd.	
0.1	17	15	29	27	30	30	13	12	HCl
1.0	16	17	28	29	32	30	12	13	
2.0	17	18	31	28	32	27	12	12	
5.0	16	18	29	—	34	29	12	17	
0.1	31	24	52	41	—	—	25	21	H_2SO_4
1.0	30	26	51	43	—	—	23	20	
2.0	28	22	51	42	—	—	22	20	
5.0	30	26	53	48	—	—	24	21	

TABLE II.

One per cent. Solutions of Fructose and α -Glucose in Acids of Varying Strength.

Acid.	Hydron concentration. Equivs. per litre.	Fructose.		α -Glucose.	
		Acid.	Neutd.	Acid.	Neutd.
$N/10\text{-HCl}$	0.0810	16	17	29	28
$N/10\text{-H}_2\text{SO}_4$	0.0660	30	24	52	43
$N/50\text{-HCl}$	0.0188	69	62*	118	97*
$N/50\text{-H}_2\text{SO}_4$	0.0160	78	75*	124	75*
$N/10\text{-H}_3\text{PO}_4$	0.0130	211	84*	238	150*
$N/10\text{-C}_2\text{H}_3\text{O}_2$	0.0012	280	20*	1,070	65*

* With precipitation.

The hydron concentrations are taken from data in Landolt and Börnstein's "Physikalische-Chemische Tabellen."

(ii) *Alcoholic Solutions.*—Some observations were made in methyl- and ethyl-alcoholic hydrogen chloride solutions in view of the considerable amount of synthetic work which has been carried out in these media. Concentrations of $N/20$ -acid were employed in order to approximate to the 0.25 per cent. hydrogen chloride solutions which have most frequently been used by E. Fischer,

Irvine, and other workers with these reagents. Very similar results were obtained to those found in aqueous solutions.

The methyl alcohol was distilled over lime and then over a little fructose, whilst the ethyl alcohol was twice distilled over lime and potassium permanganate. Ten c.c. of the neutral solvents caused precipitation in the permanganate test in six hours in the case of methyl, and in sixteen hours with ethyl, alcohol. *N*/20-Methyl-alcoholic hydrogen chloride, however, decolorised the permanganate in ninety-eight minutes, the time with *N*/20-ethyl-alcoholic hydrogen chloride being fifty-six minutes.

TABLE III.

One per cent. Solutions of Fructose and α-Glucose in Alcoholic N/20-Hydrogen Chloride.

Solvent.	hydrogen	Age.	Fructose.	α-Glucose.
<i>N</i> /20-Methyl-alcoholic chloride		0.1	7	11
		2.0	—	16
		3.0	17	—
		24.0	25	120
<i>N</i> /20-Ethyl-alcoholic chloride		0.1	6	9
		2.0	7	20
		3.0	8	10
		24.0	6	23

Alkaline Solutions.

In alkaline solutions, it is also possible to utilise the reduction of the dyes indigo and methylene-blue; the former gives two fairly definite colour stages, passing from blue through green to a clear red, and then changing to pure yellow. The times occupied from the commencement of the test in reaching the standard red and yellow tints are given in the tables under the columns headed respectively "R" and "Y."

Methylene-blue fades to a colourless solution. In both cases, the dyes are restored by contact with air, and it was found desirable to fill the upper part of the test-tubes with an inert gas, hydrogen being employed.

It was found that the stock alkaline sugar solutions, whether maintained under air or under hydrogen, behaved the same towards the three oxidising agents.

The result of neutralising the alkaline sugar solution, when the latter has been freshly prepared, is to cause a very marked retard-

ation in reducing power, but after the alkaline solution has remained for some hours, the reducing power after neutralisation becomes greater, approaching that of the alkaline solution itself in about twenty-four hours.

This shows that initially the change induced by alkali is reversed on neutralisation, but the progressive alteration in behaviour is somewhat obscure, although it may well be due to the appearance of small amounts of decomposition products resulting from more profound disturbance of the sugar molecule.

It is evident, however, that the behaviour of neutralised alkaline solutions is quite distinct from that of neutralised acid solutions, so that it may be considered that the cause of the reducing activity of the sugar is not the same in each case.

The subjoined tables give the full series of readings up to five hours for fructose, α - and β -glucose, and mannose in the presence of one and of two equivalents of sodium hydroxide (table IV). In table V are recorded the initial and final values (five hours) for fructose and α -glucose with varying concentrations of sodium hydroxide, and in table VI we quote similar data for these sugars in the presence of one equivalent of a number of aqueous alkalis.

Correlation of the Reducing Action of the Sugars with Alterations in Optical Rotatory Power.

In order to obtain a convenient polarimetric reading in the 2-dm. tubes employed, the behaviour of 5 per cent. solutions of fructose and of α -glucose was examined in neutral, acid, and alkaline media. The concentrations of the acid ($N/10\text{-HCl}$) and of the alkali ($N/18\text{-NaOH}$), and the conditions of the reducing time-tests, were otherwise maintained unaltered. The alteration in concentration of the sugars involved the determination of the corresponding times of reaction with permanganate and the dyes, and the results of these and of the observations of optical rotatory power are collected in table VII.

TABLE IV.
One per cent. Sugar Solutions with One and Two Equivalents of Aqueous Sodium Hydroxide.
(a) Tests with Potassium Permanganate.

NaOH equiv.	Age.	Fructose.			α -Glucose.			β -Glucose.			Mannose.		
		Alk.	Neutd.	Alk.	Alk.	Neutd.	Alk.	Alk.	Neutd.	Alk.	Alk.	Neutd.	Alk.
2.0	0.1	1.75	65.0*	10.0	61.0*	90.0†	—	—	—	26	66†	—	—
	1.0	1.25	60.0*	8.0	90.0†	—	—	—	—	24	120†	—	—
	3.5	0.75	8.0	3.0	150.0†	—	—	—	—	16	160†	—	—
	5.0	0.50	0.5	2.0	60.0†	—	—	—	—	14	70	—	—
	24.0	0.75	0.2	1.75	1.25	—	—	—	—	7	13	—	—
1.0	0.1	3.00	60.0†	11.0	180.0†	—	15.0	35.0†	90†	25	—	—	—
	1.0	2.00	—	7.5	—	—	11.0	60.0†	—	20	73*	—	—
	3.0	1.75	65.0	4.5	73.0*	—	9.0	48.0	—	17	46*	—	—
	5.0	1.25	11.0	3.0	48.0*	—	4.0	37.0	—	9	5	—	—
	24.0	1.25	0.25	2.5	2.5	—	4.5	4.5	—	4	—	—	—

(b) Tests with Indigo and Methylene-blue.

NaOH equiv.	Age.	Fructose.			α -Glucose.			β -Glucose.			Mannose.		
		Indigo.		Meth. Blue.	Indigo.		Meth. Blue.	Indigo.		Meth. Blue.	Indigo.		Meth. Blue.
		R.	Y.		R.	Y.		R.	Y.		R.	Y.	
2.0	0.1	1.00	2.50	1.50	4.00	6.00	7.00	—	—	—	17†	21	29
	1.0	0.75	1.25	0.50	3.25	5.50	4.00	—	—	—	12†	18	21
	3.0	0.50	1.00	0.40	2.50	5.00	3.00	—	—	—	8†	15	11
	5.0	0.50	1.25	0.35	2.25	5.00	2.25	—	—	—	7†	15	10
	24.0	1.25	3.00	2.00	2.50	5.00	3.00	—	—	—	5†	10	6
1.0	0.1	1.25	3.50	3.00	9.0	12.5	11.0	14	19	18	22†	33	37
	1.0	1.50	2.75	1.25	8.5	11.5	7.0	8	15	12	19†	30	31
	3.0	1.25	2.50	1.00	6.0	11.5	5.0	7	14	9	16†	28	24
	5.0	1.25	2.50	1.00	5.0	11.0	4.0	5	11	5	17†	28	22
	24.0	3.25	4.75	2.00	6.0	9.0	5.5	4	7	4	17†	22	24

† Precipitation set in.
‡ Indefinite end-point.

* Precipitation set in.

† Indicates end-point.

TABLE V.
One per cent. Solutions of Fructose and α-Glucose with Varying Strengths of Sodium Hydroxide.

NaOH equiv. 2.0 — 1.0 — 0.75 — 0.5 — 0.25 —	OH ion concn. per litre. 0.0978 — 0.0506 — 0.0383 — 0.0256 — 0.0129 —	Age. 0.1 5.0 0.1 5.0 0.1 5.0 0.1 5.0 0.1 5.0	Fructose.						α-Glucose.							
			Indigo.			Permanganate			Indigo.			Meth. Blue.			Permanganate.	
			R.	Y.	Meth. Blue.	Alk.	Neutd.	R.	Y.	R.	Y.	Meth. Blue.	Alk.	Neutd.		
—	—	—	1.00	2.50	1.50	1.75	65.0*	4.00	6.00	7.00	10.0	61*				
—	—	—	0.50	1.25	0.35	0.50	0.5	2.25	5.00	2.25	2.0	60†				
—	—	—	2.25	3.50	3.00	3.00	60.0†	9.0	12.5	11.0	11.0	180†				
—	—	—	1.25	2.50	1.00	1.25	11.0	5.0	11.0	4.0	3.0	48*				
—	—	—	5.0	7.5	5.0	5.0	55.0*	14.0	21.5	19.5	16.0	57*				
—	—	—	1.25	3.0	1.0	1.5	24.0	6.0	13.0	6.0	8.5	23*				
—	—	—	6.0	8.5	6.0	7.0	29.0*	20.0†	35.0	27.0	24.0	43*				
—	—	—	3.0	4.5	3.0	3.5	19.0†	14.0†	23.0	19.0	15.0	36*				
—	—	—	15.0†	20.0	17.5	14.0	50.0*	51.0†	91.0	66.0	95.0†	50*				
—	—	—	7.0†	10.0	5.0	5.0	31.0†	25.0†	50.0	25.0	33.0	31*				

* Precipitation set in.
† Indefinite end-point.

* Precipitation set in.

† Indefinite end-point.

TABLE VI.
One per cent. Solutions of Fructose and α -Glucose with One Equivalent of Various Alkalis.

Alkali.	OH ion concn. per litre	Age.	Fructose.					α -Glucose.				
			Indigo.			Permanganate.		Indigo.			Permanganate.	
			R.	Y.	Meth. Blue.	Alk.	Neutd.	R.	Y.	Meth. Blue.	Alk.	Neutd.
NaOH	0.0506	0.1 5.0	2.25 1.25	3.50 2.50	3.00 1.00	3.00 1.25	60† 11	9.0 5.0	12.5 11.0	11.0 4.0	11.0 3.0	180† 48†
KOH	0.0508	0.1 5.0	4.50 0.75	6.00 2.50	5.00 0.75	4.00 1.25	120† 60	13.0 5.0	20.0 10.0	18.0 6.0	16.0 5.0	20* 60
Ba(OH) ₂	0.0478	0.1 5.0	5.00 1.00	6.00 1.50	5.00 1.25	4.00 1.25	— —	15.0† 4.0	18.0 6.5	18.0 5.0	16.0 4.0	— —
Na ₂ CO ₃ (Hydrolysis)	0.0024	0.1 5.0	† †	83.0 56.0	150.0 98.0	30.0† 16.0	61* 20*	Practically unchanged.				
K ₂ CO ₃ (Hydrolysis)	?	0.1 5.0	† †	57.0† 49.0†	88.0† 60.0	42.0† 27.0	39* 27*	Practically unchanged.				
NH ₄ OH	0.0011	0.1 5.0	Very little action.			70.0 48.0	19* 60†	Practically unchanged.				

† Indefinite end-point.

* Precipitation set in.

TABLE VII.
Comparison of Rotatory Power with reducing Action of Sugars in 5 per cent. Solution.
 (a) *Neutral Solutions.*

Age in hours.	Fructose.			Glucose.			β -Glucose.		
	Permanganate.	[α] _D .		Permanganate.	[α] _D .		Permanganate.	[α] _D .	
0.1	24 hours. Almost colourless	-104.2°		23 hours. Still yellow	+96.8°		6 hours. Almost colourless	+27.5°	
0.5	—	92.5		—	—		—	33.8	
1.0	24 hours. Almost colourless	91.5		22 hours. Still yellow	88.2		6 hours. Pale yellow	37.8	
2.0	24 hours. "	91.2		—	—		—	44.5	
3.0	—	—		—	—		—	—	
3.5	—	—		22 hours. Still yellow	52.0		—	—	
4.0	—	91.2		—	—		20 hours. Clear.	49.2	
5.0	—	—		—	51.5		—	49.2	
6.0	—	91.2		—	—		—	49.0	
24.0	48 hours. Almost colourless	91.2		Clear before 24 hours.	50.7		Clear before 24 hours.	49.5	

TABLE VII. (continued).
(b) Solutions in N/10-Hydrochloric Acid.

Age in hours.	Fructose.				Glucose.				β -Glucose.			
	Permanganate.		[α].	Neutd.	Permanganate.		[α].	Neutd.	Permanganate.		[α].	Neutd.
	Acid.	8			Acid.	21			Acid.	13		16
0.1	8	—	-91.2°	—	21	21	+91.8°	—	—	—	+30.5°	—
0.5	—	—	91.5	—	—	—	—	—	—	—	43.5	—
1.0	8	6½	91.5	—	21	20	51.2	—	13	14	49.8	—
2.0	7	6½	91.0	—	—	—	—	—	—	—	—	—
3.0	—	—	—	—	—	—	—	—	12½	20	49.5	—
3.5	—	—	—	—	18	20	49.8	—	—	—	—	—
4.0	7½	8	91.0	—	—	—	—	—	—	—	49.5	—
5.0	—	—	—	—	17	16½	49.8	—	13	25	49.5	—
6.0	—	—	90.8	—	—	—	—	—	—	—	—	—
24.0	8	10	90.8	—	20	14	49.8	—	14	20	49.5	—

TABLE VII. (continued).

(c) Solutions in N/18-Sodium Hydroxide.

Age in hours.	Fructose.						Glucose.						β-Glucose.									
	Indigo.			Permanganate.			[α] _D .	Indigo.			Permanganate.			[α] _D .	Indigo.			Permanganate.			[α] _D .	
	R.	Y.	Meth. Blue.	Alk.	Neutd.	R.		Y.	Meth. Blue.	Alk.	Neutd.	R.	Y.		Meth. Blue.	Alk.	Neutd.	R.	Y.	Meth. Blue.		Alk.
0.1	2.0	3.5	3.0	3.0	21	-89.7°	[α] _D .	12	17½	15½	16½	30	+43.2°	[α] _D .	19	24	23	18	64	+49.2°	[α] _D .	
0.5	—	—	—	—	—	89.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
1.0	1.75	3.5	1.5	2.5	16	88.0	—	9	14	12	13	25	46.7	—	9	15	13	9	40	40.0	—	
2.0	1.75	2.5	1.5	2.0	15	86.7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
3.0	—	—	—	—	—	—	—	5	11	7	7	16½	45.2	—	6½	11	8	6½	35	—	—	
4.0	1.25	1.75	1.25	1.6	14½	84.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
5.0	—	—	—	—	—	—	—	3	6	4	4	15	42.5	—	6	11	6½	6	35	44.2	—	
6.0	1.0	1.5	1.0	1.5	9½	83.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
24.0	1.75	2.25	2.0	1.5	1.0	81.5	—	3	7½	5	5	4	34.5	—	5	11	7½	8	6	39.2	—	
Age in days.																						
2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
4	—	—	—	—	—	49.5	—	—	—	—	—	—	30.2	—	—	—	—	—	—	—	33.0	
8	—	—	—	—	—	—	—	—	—	—	—	—	23.2	—	—	—	—	—	—	—	23.5	
12	—	—	—	—	—	—	—	—	—	—	—	—	10.0	—	—	—	—	—	—	—	10.0	
25	—	—	—	—	—	-4.2	—	—	—	—	—	—	+3.8	—	—	—	—	—	—	—	+6.7	

One per cent. Solutions of Fructose and Glucose in Pyridine.

In view of the interest attaching to the action of pyridine on the sugars, a few experiments were made with solutions of the two sugars in pure pyridine at 25°.

The pyridine was twice distilled over lime before use and boiled at 116–116·5°. Ten c.c. of the distilled pyridine caused no alteration in the blue tint of indigo or of methylene-blue (2 c.c. of the standard dye solutions) in twenty-four hours, but with 2 c.c. of *N*/100-permanganate a precipitate appeared in three hours.

The 1 per cent. fructose and glucose solutions in pyridine were also without action on the dyes, but results analogous to those of the weaker alkalis were obtained with permanganate. These are given in table VIII, in which the age of the solutions is in hours and the decolorisation times in minutes, as usual.

TABLE VIII.

One per cent. Solutions of Fructose and of α-Glucose in Pyridine.

Ago.	Fructose.	α-Glucose.
0·1	30 not quite colourless	56 with very fine precipitation.
1·0	23 " "	40 " " " "
2·0	17 " "	" " " "
3·5	" "	35 " " " "
4·2	12 " "	" " " "
5·0	" "	30 " " " "
6·0	8 " "	" " " "

Comparative Experiments with Simple Aldehydes and Derivatives of Ethylene Oxide.

Some experiments were made on the reducing action of aqueous solutions of acetaldehyde, *n*-butaldehyde, acetone, and epichlorohydrin and ethylene oxide. In neutral 1/18th gram-molecular solution all these substances, with the exception of acetone, caused the pink colour of the permanganate in our standard test to disappear within about two hours, but the resulting clear orange solution underwent no further change in colour for many hours. In the case of acetone, the pink tint did not entirely vanish for several hours.

The results of the permanganate tests in *N*/10-hydrochloric acid solution are given in the next table; in the case of ethylene oxide, the exact concentrations were not accurately known, but tests were made with two strengths, approximately gram-molecular per litre and 1/18th gram-molecular per litre.

TABLE IX.

*Solutions of Aldehydes and of Ethylene Oxides in
N/10-Hydrochloric Acid.*

Substance.	Concn. per litre.	Age.	Permanganate tests.	
			Acid.	Neutralised.
Acetaldehyde ...	M/18	0.1	6½ hrs. Pale yellow	9 minutes, with pptn.
		1.0	6½ hrs. " "	7 " "
		3.0	2 hrs. " "	10 " "
n-Butaldehyde ...	M/18	0.1	3½ hrs. Pale yellow	13 minutes, with pptn.
		1.0	2½ hrs. " "	10 " "
		3.5	2½ hrs. " "	10 " "
		24.0	2½ hrs. " "	10 " "
Epichlorohydrin	M/18	0.1	140 minutes.	82 minutes.
		1.5	120 "	53 "
		4.3	90 "	35 "
		24.0	120 "	32 "
Ethylene oxide ...	M/18	0.1	103 minutes.	80 minutes.
		1.0	132 "	89 "
		3.0	130 "	80 "
		23.0	110 "	20 "
	M	0.1	8 minutes.	10 minutes.
		1.0	12 "	13 "
		2.0	17 "	14 "
		5.0	16 "	14 "
		23.0	15 "	14 "

Table X illustrates the data obtained in N/18-aqueous sodium hydroxide; with both aldehydes, acetone, and epichlorohydrin and ethylene oxide, indigo passed rapidly through green to a pale yellow colour, and the original blue tint could not be restored by shaking the yellow solution with air. It appears, therefore, that some action was proceeding in these cases beyond simple reduction to indigo-white, and the colour test is not valid in this instance.

TABLE X.

Solutions of Aldehydes and of Ethylene Oxides in N/18-Sodium Hydroxide.

Substance.	Concn. per litre.	Age.	Methylene- blue.	Permanganate.	
				Alkaline.	Neutralised.
Acetaldehyde	M/18	0.1	60†	11*	11*
		1.0	32†	6*	50
		3.5	21†	16*	30
		5.0	23†	16*	18
		23.0	35†	6*	1

* Precipitation set in.

† Indefinite end-point.

TABLE X. (continued).

Solutions of Aldehydes and of Ethylene Oxides in N/18-Sodium Hydroxide.

Substance.	Concn. per litre.	Age.	Methylene- blue.	Permanganate.	
				Alkaline.	Neutralised.
<i>n</i> -Butaldehyde.....	<i>M</i> /18	0.1	39†	8*	8*
		1.0	20	5*	8*
		3.5	14	7*	7*
		5.0	12	8*	8
		23.0	13	19*	2
Acetone.....	<i>M</i> /18	0.1			
		1.3			
		3.3	Permanent.	Pale green, then turbid yellow.	In 16 hours, precipitation, but still pink.
		5.3			
		23.0			
Epichlorohydrin	<i>M</i> /18	0.1	Permanent.	113*	207
		1.5	"	100*	140
		4.3	"	95*	116
		24.0	"	80*	110
Ethylene oxide	<i>M</i> /18	0.1	Permanent.	245†	352
		1.0	"	236†	350
		3.0	"	220†	340
		23.0	"	174†	320
	<i>M</i>	0.1	Permanent.	76†	87
		1.0	"	77†	84
		2.0	"	71	88
		5.0	"	55	77
		23.0	"	19*	53

* Precipitation set in.

† Indefinite end-point.

The most interesting points in this series of experiments are:

(i) The alkaline solutions of the aldehydes reduce methylene blue similarly to the sugars, and there is some similarity in their behaviour to alkaline permanganate.

(ii) The ethylene oxide derivatives show no similarity to the sugars in alkaline solution, either with respect to permanganate or to methylene-blue.

(iii) On the other hand, the acid solutions of the ethylene oxide compounds display great likeness to those of acid sugar solutions both in the "acid" and "neutralised" permanganate tests.

WARRINGTON.

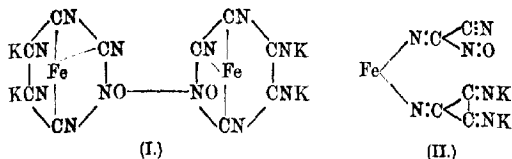
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CCXXXIV.—*The Constitution of the Nitroprussides.*
Part I. Conductivity and Cryoscopic Measurements.

By GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER.

FROM time to time, the nitroprussides have been made the subject of considerable speculation, but little attempt has been made to verify experimentally the various constitutions assigned to them.

Hofmann, who is responsible for most of the experimental work in this field (*Annalen*, 1900, 312, 1), assigned to sodium nitroprusside the co-ordination formula $[\text{Fe}(\text{CN})_5\text{NO}]\text{Na}_2$. Friend (T., 1916, 109, 721), apparently without further experimental work, proposed for potassium nitroprusside the formula (I).



This formula corresponds with the empirical one given in works of reference (for example, Moissan, "Traité de chimie minérale," 1905, 417), which formula, however, seems never to have had any evidence in its favour.

Friend at the same time rejected the formula (II) suggested by Browning (T., 1900, 77, 1238) for potassium nitroprusside, in view of his theory as to the constitution of the ferrocyanides, which theory has since been shown to be unnecessary (Bennett, T., 1917, 111, 490).

It was suggested by one of us (T., 1916, 109, 1130) that a determination of the molecular weights of some nitroprussides would throw light on the problem, and, as a result, a number of nitroprussides have been prepared and investigated cryoscopically and their conductivities measured. From the results so obtained, the number of ions present in a solution of a nitroprusside has been calculated, and conclusions have been drawn as to the molecular weights of the salts in question. In these experiments, the degree of dissociation of the salt at any particular dilution was found in the usual way by dividing the molecular conductivity at that dilution by its value at infinite dilution. From cryoscopic measurements, the molecular depression of the freezing point of water was found for various concentrations of the salt, and by dividing this number by 18.7 (the molecular constant for water), the value for

i (the van't Hoff coefficient) was obtained. The number of ions, k , into which each molecule of the salt dissociates was then obtained by substituting the experimental values of a and i in the equation

$$i = 1 + (k - 1)a.$$

A similar method was used by Petersen (*Zeitsch. physikal. Chem.*, 1902, **39**, 249) in connexion with the cobaltammines. This author was of the opinion that the conclusions drawn by Werner (*Zeitsch. physikal. Chem.*, 1893, **12**, 35, etc.) from measurements of the molecular conductivity at a dilution of 1000 litres (not necessarily at infinite dilution) were in most cases inaccurate.

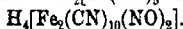
The figures given by Jones (*Carnegie Institute of Washington, Publication No. 170*) for the molecular conductivities of a large number of salts show that most salts are completely dissociated at dilutions of about 1000 litres. In some cases, however, the molecular conductivity again increases beyond that dilution, owing to causes other than dissociation. From the figures given by Petersen (*loc. cit.*) for the conductivity of the cobaltammines, it would appear that similar difficulties arose in his work.

In the present investigation, the substances considered are salts of a strong acid. (This has been found to be the case from a preliminary examination of the molecular conductivity of nitroprussic acid itself.) The conductivities of the salts were determined for solutions diluted to 2048 litres, and the values were plotted against the concentrations. The value for infinite dilution was found by extrapolation from the curve so obtained. In all cases, the value of μ_{∞} differs only slightly from the value actually found for μ_{1024} , a result which was expected from the nature of the salts in question.

In the following tables are given the values of k calculated on the assumption that the nitroprussides are represented by the simple formula $M_3/[Fe(CN)_5NO]$, which will be referred to in future as type I. In addition, the value of k_1 has been calculated in each case for a molecule, $M_4/[Fe_3(CN)_{10}(NO)_2]$ (type II).

In the case of a univalent cation, a molecule of type I will dissociate into three ions, type II giving five ions. The value of k should therefore approximate to 3 if formula I is correct, whilst if II is correct, $k_1 = 5$. In the same way, a salt of a bivalent cation should give the values $k = 2$ or $k_1 = 3$.

It is considered that the results obtained show conclusively that all the nitroprussides examined conform to the simple formula (type I). They are salts of $H_2[Fe(CN)_5NO]$, and not of



The possible effect due to hydration of the ions has not been overlooked (compare Jones, *Carnegie Institute of Washington, Publi-*

cation No. 180), and it is considered that the conclusions drawn from the figures obtained in the present work cannot be regarded as vitiated on this ground. Whereas hydrate formation may account for the differences between the experimental and absolute values of k , the extremely large differences in the case of k_1 cannot be accounted for in this way.

It is hoped in a future communication to describe the alkyl nitroprussides, some of which have been prepared, although in an impure state only.

EXPERIMENTAL.

The conductivity measurements were all made at 25.0°. The degree of dissociation of salts at 0° differs only slightly from that at 25°, and the latter temperature allows of greater accuracy in determining the conductivity. In the following tables, v is the number of litres containing one gram-molecule of the salt (calculated for the simple formula I), μ is the molecular conductivity, a is the degree of dissociation and is equal to μ_0/μ_∞ , Δ_t is the observed depression of the freezing point of water, $M\Delta_t$ is the molecular depression and is equal to $v \times \Delta_t \times 10$, i is the van't Hoff coefficient and is equal to $M\Delta_t/18.7$, and k is the number of ions into which a molecule dissociates, and is obtained from the equation $i=1+(k-1)a$; k_1 is the corresponding value of k calculated for a molecule of type II by doubling i and then substituting in the equation $i=1+(k_1-1)a$.

The values of a in the cryoscopic tables are taken from the curves obtained from conductivity data.

Sodium Nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$.

The salt used was a pure specimen.

Conductivity Measurements.

v .	μ .	a .
4	155.2	0.63
8	169.4	0.69
16	181.8	0.74
32	194.3	0.79
64	204.9	0.84
128	214.2	0.87
256	222.0	0.91
512	229.2	0.94
1024	236.2	0.96
2048	244.6	—
∞	245.0	—

Cryoscopic Measurements.

v	Δ_r	$M\Delta_r$	i	$a = \mu_r/\mu_\infty$	k	k_1
47.1	0.115	54.1	2.90	0.81	3.35	6.9
24.4	0.218	53.2	2.84	0.77	3.40	7.1
14.55	0.345	50.2	2.68	0.73	3.30	7.0
10.81	0.456	49.3	2.64	0.71	3.30	7.0
8.76	0.560	49.1	2.62	0.70	3.31	7.0
7.12	0.678	48.3	2.58	0.68	3.32	7.1

Type I requires $k=3$. Type II requires $k_1=5$.

Potassium Nitroprusside, $K_2[Fe(CN)_5NO]$.

This salt was prepared by decomposing the barium salt with the calculated weight of pure potassium sulphate, filtering off the barium sulphate, and evaporating the filtrate at a low temperature under diminished pressure. The residue so obtained was crystallised from aqueous alcohol containing about 95 per cent. of alcohol. It crystallises in pale pink crystals without water of crystallisation:

0.4010 gave 0.1076 Fe_2O_3 . $Fe=18.8$.

$C_5ON_6FeK_2$ requires $Fe=19.0$ per cent.

Conductivity Measurements.

v	μ	a
8	199.2	0.745
16	205.2	0.795
32	215.7	0.836
64	227.2	0.881
128	236.6	0.917
256	244.0	0.946
512	249.3	0.966
1024	257.0	0.996
2048	258.1	—
∞	258.0	—

Cryoscopic Measurements.

v	Δ_r	$M\Delta_r$	i	$a = \mu_r/\mu_\infty$	k	k_1
34.4	0.150	51.6	2.76	0.85	3.07	6.32
24.1	0.213	51.3	2.74	0.82	3.12	6.46
14.66	0.316	48.3	2.48	0.79	2.87	6.01
11.65	0.405	47.2	2.52	0.77	3.00	6.25
7.02	0.641	45.0	2.41	0.74	2.91	6.16
4.78	0.909	43.4	2.32	0.71	2.86	6.11

Type I requires $k=3$. Type II requires $k_1=5$.

Barium Nitroprusside, $Ba[Fe(CN)_5NO] \cdot 3H_2O$.

This salt was prepared by precipitating a solution of the sodium salt with zinc sulphate and boiling the zinc salt so obtained with a suspension of precipitated barium carbonate. The filtered solution of the barium salt was evaporated under diminished pressure

THE CONSTITUTION OF THE NITROPRUSSIDES. PART I. 1433

at a low temperature, and the salt crystallised from aqueous alcohol:

0.8344 gave 0.4734 BaSO_4 . $\text{Ba}=33.4$.

$\text{C}_5\text{ON}_6\text{BaFe}, 3\text{H}_2\text{O}$ requires $\text{Ba}=33.7$ per cent.

The anhydrous salt was found to be extremely hygroscopic.

Conductivity Measurements.

<i>v.</i>	μ .	<i>a.</i>
8	152.9	0.63
16	165.9	0.68
32	177.1	0.73
64	190.7	0.79
128	203.0	0.84
256	216.2	0.89
512	223.6	0.92
1024	236.9	0.98
2048	240.5	—
∞	243.0	—

Oryoscopic Measurements.

<i>v.</i>	Δ_i .	$M\Delta_i$.	<i>i.</i>	$a=\mu_v/\mu_\infty$.	<i>k.</i>	k_1 .
37.7	0.093	35.1	1.88	0.74	2.19	4.73
16.5	0.180	29.7	1.59	0.68	1.87	4.21
9.87	0.285	28.1	1.50	0.64	1.78	4.13
6.67	0.413	27.6	1.47	0.61	1.77	4.18
4.73	0.575	27.2	1.45	0.59	1.76	4.22

Type I requires $k=2$. Type II requires $k_1=3$.

This salt is of especial interest, owing to the rough equality in weights of the anion and cation.

Ammonium Nitroprusside, $(\text{NH}_4)_2[\text{Fe}(\text{CN})_5\text{NO}]$.

This salt was obtained by decomposing the barium salt with an equivalent weight of ammonium sulphate, filtering, evaporating under diminished pressure, and crystallising from aqueous alcohol, when reddish plates, very readily soluble in water, were obtained:

0.2390 gave 0.0768 Fe_2O_3 . $\text{Fe}=22.5$.

$\text{C}_5\text{ON}_6\text{Fe}(\text{NH}_4)_2$ requires $\text{Fe}=22.2$ per cent.

Conductivity Measurements.

<i>v.</i>	μ .	<i>a.</i>
16	206.7	0.77
32	218.0	0.82
64	228.5	0.85
128	236.7	0.89
256	245.6	0.92
512	251.2	0.94
1024	261.3	0.98
2048	266.2	—
∞	268.0	—

Cryoscopic Measurements.

v .	Δt .	$M\Delta t$.	i .	$a = \mu_1/\mu_\infty$.	k .	k_1 .
26.3	0.214	58.4	3.01	0.80	3.51	7.27
10.73	0.450	48.3	2.58	0.74	3.14	6.62
6.68	0.704	47.0	2.61	0.69	3.19	6.83

Type I requires $k=3$. Type II requires $k_1=5$.

Methylammonium Nitroprusside, $(\text{MeNH}_2)_2[\text{Fe}(\text{CN})_5\text{NO}]$.

This salt and the nitroprussides of di- and tri-methylamine were obtained by treating a solution of the free acid (obtained from the barium salt and the calculated sulphuric acid) with a slight excess of an alcoholic solution of the amine. The solution so obtained was evaporated under diminished pressure, and the solid residue crystallised from alcohol. The alkylammonium nitroprussides crystallise in reddish plates, which are very readily soluble in water. In appearance they resemble the barium or ammonium salts:

0.1117 gave 0.0306 Fe_2O_3 . $\text{Fe}=19.2$.

$\text{C}_5\text{ON}_6\text{Fe}(\text{MeNH}_2)_2$ requires $\text{Fe}=20.0$ per cent.

Conductivity Measurements.

v .	μ .	α .
32	185.2	0.77
64	197.7	0.82
128	208.0	0.87
256	218.5	0.91
512	225.8	0.94
1024	233.4	0.97
∞	240.0	—

Cryoscopic Measurements.

v .	Δt .	$M\Delta t$.	i .	$a = \mu_1/\mu_\infty$.	k .	k_1 .
36.6	0.148	54.2	2.90	0.78	3.45	7.2
19.05	0.262	49.0	2.67	0.71	3.35	7.1
14.15	0.339	48.0	2.57	0.68	3.31	7.1
10.13	0.466	47.2	2.52	0.62	3.45	7.5
8.35	0.541	45.2	2.42	0.59	3.41	7.5

Type I requires $k=3$. Type II requires $k_1=5$.

Dimethylammonium Nitroprusside, $(\text{Me}_2\text{NH})_2[\text{Fe}(\text{CN})_5\text{NO}]$.

0.1028 gave 0.0272 Fe_2O_3 . $\text{Fe}=18.5$.

$\text{C}_5\text{ON}_6\text{Fe}(\text{Me}_2\text{NH})_2$ requires $\text{Fe}=18.1$ per cent.

Conductivity Measurements.

	μ .	a .
16	156.5	0.68
32	172.1	0.75
64	185.2	0.81
128	196.3	0.85
256	205.8	0.90
512	212.5	0.92
1024	220.2	0.96
2048	227.3	—
	230.0	—

Cryoscopic Measurements.

v .	Δ_c .	$M\Delta_c$.	i .	$a=\mu_i/\mu_\infty$.	k .	k_1 .
35.2	0.149	52.4	2.80	0.76	3.37	7.05
16.4	0.294	48.1	2.57	0.68	3.31	7.09
8.84	0.500	44.2	2.36	0.61	3.23	7.10
5.92	0.714	42.3	2.26	0.57	3.21	7.20

Type I requires $k=3$. Type II requires $k_1=5$.

Trimethylammonium Nitroprusside, $(\text{Me}_3\text{NH})_2[\text{Fe}(\text{CN})_5\text{NO}]$.

0.2234 gave 0.0512 Fe_2O_3 . $\text{Fe}=16.0$.

$\text{C}_5\text{ON}_6\text{Fe}(\text{Me}_3\text{NH})_2$ requires $\text{Fe}=16.7$ per cent.

Conductivity Measurements.

v .	μ .	a .
16	137.1	0.65
32	154.0	0.73
64	167.3	0.80
128	183.0	0.86
256	191.7	0.90
512	201.1	0.95
1024	208.0	0.98
2048	210.5	—
∞	212.0	—

Cryoscopic Measurements.

v .	Δ_c .	$M\Delta_c$.	i .	$a=\mu_i/\mu_\infty$.	k .	k_1 .
39.0	0.134	52.2	2.79	0.75	3.39	7.11
14.47	0.290	42.0	2.24	0.63	2.97	6.52
6.56	0.588	38.6	2.06	0.50	3.12	7.24

Type I requires $k=3$. Type II requires $k_1=5$.

THE UNIVERSITY CHEMICAL LABORATORIES,
SYDNEY.

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CXXXV.—*The Propagation of Flame in Complex Gaseous Mixtures. Part I. Limit Mixtures and the Uniform Movement of Flame in such Mixtures.*

By WILLIAM PAYMAN.

IN order that flame may propagate through a mixture of an inflammable gas with air or oxygen, the heat developed by a given "layer" on burning must be sufficient to raise the contiguous layer of unburnt gas to its ignition temperature. In a "limit mixture" there is just sufficient, and only just sufficient, heat developed to accomplish this. If limit mixtures of two or more inflammable gases be mixed together, this heat balance should remain unaltered provided that all of the limit mixtures are of the same kind, that is to say, all lower-limit or all upper-limit mixtures. It follows that all mixtures, in any proportions, of limit mixtures should remain limit mixtures, the limiting percentage being that of the mixed inflammable gas. Conversely, any limit mixture of a complex inflammable gas will consist of a number of limit mixtures of the individual gases it contains.

Assuming this reasoning to be correct, imagine a limit mixture with air of a complex inflammable gas. Let A, B, C, \dots be the simple constituents of this inflammable gas, and their limits of inflammability, N_A, N_B, N_C, \dots respectively. Suppose also that the complex limit mixture contains a per cent. of A , b per cent. of B , c per cent. of C , \dots . Then this limit mixture will contain

$$aA + bB + cC + \dots + [100 - (a + b + c + \dots)] \text{air.}$$

This limit mixture, *ex hypothesi*, comprises a series of limit mixtures of the simple inflammable gases. In such a simple limit mixture of A , for example, every N_A parts of A are associated with $100 - N_A$ parts of air, so that every a parts of A are associated with $\left(\frac{100 - N_A}{N_A}\right)a$ parts of air. Similarly, for B, C, \dots

The complex limit mixture will therefore contain

$$a + \left(\frac{100 - N_A}{N_A}\right)a, \quad b + \left(\frac{100 - N_B}{N_B}\right)b, \quad c + \left(\frac{100 - N_C}{N_C}\right)c, \dots$$

Since these terms are expressed as percentages, they will together equal 100, so that

$$a + \left(\frac{100 - N_A}{N_A}\right)a + b + \left(\frac{100 - N_B}{N_B}\right)b + c + \left(\frac{100 - N_C}{N_C}\right)c + \dots = 100.$$

This expression, on simplification, becomes

$$\frac{a}{N_A} + \frac{b}{N_B} + \frac{c}{N_C} + \dots = 1.$$

This is the formula of Le Chatelier, which has been shown to apply accurately for both the upper and lower limits of inflammability of a number of complex gaseous mixtures with air (Coward, Carpenter, and Payman, this vol., p. 27).

This "formula," but not the generalisation from which it has been deduced, applies only to mixtures of inflammable gases with an atmosphere of constant composition, such as air. For the numerical quantities involved in the formula relate to the combustible gases only, and admit of no allowance being made for variations in the proportions of inert gas present. The generalisation, however, should hold good for all limit mixtures; for mixtures in which the proportion of inert gas is greater or less than in air, or even in which its proportion is not constant.*

The effect of an inert gas (nitrogen) on the limits of inflammability of methane has been investigated by Burgess and Wheeler (T., 1914, 105, 2596), who determined the limits for this gas in several artificial atmospheres of oxygen and nitrogen containing less oxygen than air. During the course of the present inquiry into the mode of combustion of mixed gases, it became necessary to extend their work to include atmospheres containing more oxygen than air, and pure oxygen.

The method of experiment used by Burgess and Wheeler, which involved the central ignition of the mixtures in a large globe, was not employed in the present research. This investigation is mainly concerned with the uniform movement of flame, and the determinations of the limits were made in the same apparatus as was used for measuring the speed of propagation of flame. This consisted of a horizontal glass tube 2.5 cm. in diameter, open at one end and closed at the other, the mixtures being ignited close to the open end of the tube by means of an electric spark. The criterion of inflammability was, therefore, the horizontal propagation of flame throughout the length of the tube.

The determinations were carried out by the method of trial and error, using mixtures which differed in composition by about 0.10 per cent. of methane. Throughout this paper, the term "limit mixture," whether upper or lower, implies that mixture in which flame was just able to propagate.

The results of the determinations are given in table I. The limits were always sharply defined. On sparking a mixture con-

This will be described in future as the "limits generalisation."

taining a little less than the lower-limit percentage of inflammable gas, there usually arose a ball of flame which travelled some 5 or 6 cm. along the tube. A mixture containing slightly more inflammable gas than the higher-limit percentage usually produced a flame which travelled the short distance from the spark to the open end of the tube, owing to the dilution of the mixture there by diffusion of the outside air. In the limit mixtures, flame travelled steadily and at an approximately uniform speed throughout the length of the tube.

In no instance did the flame of the burning limit mixture fill the whole cross-section of the tube, but it was usually similar to the trailing flames described by Burgess and Wheeler (T., 1914, 105, 2593). This was most marked with the upper-limit mixtures and with the lower-limit mixture of methane in pure oxygen. These flames were about 10 mm. in diameter and about 15 mm. long, and had a short tail, resembling a "Prince Rupert's drop" in shape.

In three instances the deposition of carbon was noticed during the passage of flame through a limit mixture, namely, in the upper-limit mixtures of methane with atmospheres containing 50, 66, and 100 per cent. of oxygen.* The flames resembled that of a tallow candle, and the odour of the residual gases was similar to that caused by the smouldering wick of such a candle. In general, the upper-limit flames were olive-green in colour. The colour of the lower-limit flames was pale blue.

TABLE I.

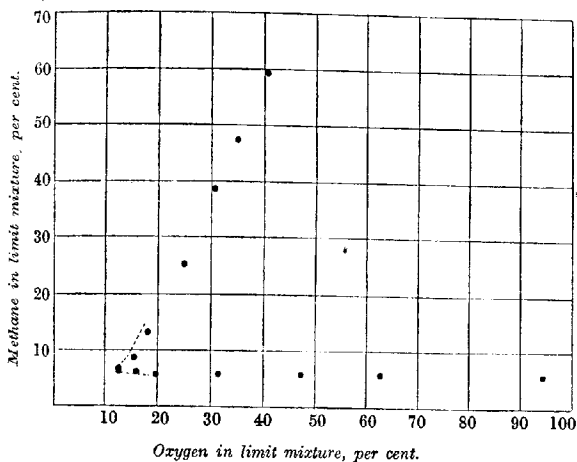
The Limits of Inflammability of Methane in Mixtures of Oxygen and Nitrogen.

Percentage of oxygen in atmosphere.	Lower limit.			Upper limit.		
	CH ₄ .	O ₂ .	N ₂ .	CH ₄ .	O ₂ .	N ₂ .
13.7	6.4	12.8	80.8	6.9	12.7	80.4
17.0	6.1	16.0	77.9	8.9	15.5	75.6
21.0 (air)	5.8	19.8	74.4	13.3	18.2	68.5
33.0	5.8	31.4	62.8	25.1	25.0	49.9
50.0	5.8	47.1	47.1	38.8	30.6	30.6
66.0	5.8	62.8	31.4	47.5	35.0	17.5
100.0	5.7	94.2	—	59.2	40.8	—

* According to Bone (*Phil. Trans.*, 1915, 215, 275), when methane and oxygen mixtures are exploded under pressure, "there is a total cessation of any separation of carbon (which is very marked with mixtures $2\text{CH}_4 + \text{O}_2$) after the proportion of oxygen in the original mixture exceeds the limit $3\text{CH}_4 + 2\text{O}_2$." No carbon was deposited when a mixture containing 59.3 per

The results are plotted in the diagram, the ordinates representing percentages of methane and the abscissae percentages of oxygen in the limit mixtures.

If the "limits of generalisation" given earlier in this paper applies to these mixtures, the values for each of the two sets of limits should lie on a straight line. It will be seen that this holds accurately over a large range of mixtures, namely, over those containing more than about 17 per cent. of oxygen.* Mixtures containing less than this amount of oxygen require rather more methane than the theoretical quantities to attain both the upper and lower limits.



The dotted lines in the diagram represent the values obtained by Burgess and Wheeler (*loc. cit.*). The shapes of both curves are

cent. of methane and 40.7 per cent. of oxygen was exploded under a pressure of 12.7 atmospheres.

In the present series of experiments, at atmospheric pressure, a mixture of approximately the same composition as that used by Bone (59.2 per cent. of methane and 40.8 per cent. of oxygen) deposited carbon, as did also mixtures containing less oxygen in proportion to the methane present, namely, those intermediate in composition between $3\text{CH}_4 + 2\text{O}_2$ and $\text{CH}_4 + \text{O}_2$. It would therefore appear that the limiting composition at which the deposition of carbon ceases is not fixed, but varies with the initial pressure of the mixture.

* According to Burgess and Wheeler (*loc. cit.*), no mixture of methane, oxygen, and nitrogen is capable of propagating flame when there is less than about 13 per cent. of oxygen present.

similar, the difference in magnitude being due to the difference in experimental conditions.

Little change was observed in the lower limit until the mixtures contained a large excess of nitrogen; whilst the value with pure oxygen was only slightly lower than that with air. The latter observation is not in agreement with the results recorded by Parker (T., 1914, 105, 1002), who found the lower limit of inflammability of methane to be slightly higher with oxygen than with air (6.0 per cent. and 5.8 per cent. respectively). The apparatus used by Parker was similar to that previously used by Burgess and Wheeler, namely, a 2-litre globe in which the mixtures were ignited at the centre.

This lack of agreement is undoubtedly due to the difference in the position of the point of ignition in the two sets of experiments. It has frequently been noted that the limits of inflammability vary with the position of the point of ignition according as the flame has to pass upwards or downwards through the gas mixture. The fact that a flame will pass more readily upwards than downwards is well illustrated when a lower-limit mixture of methane in air, for example, is ignited by a spark at the centre of a globe. As soon as the spark passes, a flame shoots to the top of the vessel, bends over, and then moves slowly downwards to the bottom.

In order to investigate this point further, a series of experiments was carried out to determine quantitatively the effect of varying the point of ignition on the limits of inflammability of methane in air and in oxygen. A glass tube 2.5 cm. in diameter was used, closed at one end and fitted with firing points at the other (open) end.

TABLE II.

Limits of Inflammability of Methane with Different Positions of the Point of Ignition.

Mode of propagation.	Percentage of methane in lower-limit mixture.	
	Air.	Oxygen.
Upward	5.5	5.4
Horizontal	5.9	5.8
Downward	6.1	6.3
Central ignition (Parker)...	5.8	6.0

Both for upward and horizontal propagation the lower limit of inflammability of methane is less in oxygen than in air. For downward propagation, however, the order is reversed. The differences observed are not very great, although too large to be accounted for by experimental error. Of the factors which determine the value of the limiting percentage of inflammable gas, the

transference of heat by convection and the absorption of heat by the mixture may be mutually opposed. During the downward propagation of flame, convection does not materially affect the transference of heat to unburnt layers of the mixture; the influence of the slightly higher specific heat of oxygen as compared with that of nitrogen therefore becomes apparent. With horizontal and upward propagation of flame, however, the influence of convection currents masks the effect of the higher specific heat of oxygen.

The change of order of the results, dependent on the direction of travel of the flame, is more marked when the results for methane in air are compared with those for hydrogen. Such a comparison is made in table III.

TABLE III.

Lower Limits of Inflammability in Air of Methane and of Hydrogen.

Mode of propagation.	Percentage of inflammable gas	
	Methane.	Hydrogen.
Upward	5.5	4.2
Horizontal	5.9	6.2
Downward	6.1	9.7
Central ignition	5.8	9.2

Attempts have been made to calculate the limits of inflammability of a gas from its thermal constants. It will be clear from a consideration of the results recorded in table III that any such calculation is doomed to failure unless allowance can be made for the influence of convection currents.

Since the lower limit of inflammability of methane (downward propagation of flame) is less with air than with oxygen, it might be expected to be less still with an atmosphere containing less oxygen than air. This, however, is not so. The lower limit of inflammability of methane in an atmosphere containing 17 per cent. of oxygen was found to be 6.3 per cent. for downward propagation of flame. This limit is thus affected in the same sense as both limits for horizontal propagation in mixtures containing only a small percentage of oxygen; that is to say, more methane is required to form the limit mixture than would be expected from results with mixtures richer in oxygen.

This displacement of the range of inflammability corresponds with the displacement of the range for maximum speed of uniform movement of flame in mixtures of methane and air. It has been generally assumed that the latter displacement is due to the higher thermal conductivity of methane as compared with that of air. A

similar displacement is found, however, when the inflammable gas has a thermal conductivity less than that of air, as will be shown in a subsequent communication. The displacement under consideration in the present paper, and other similar displacements, have one feature in common, namely, that the mixtures contain a large proportion of inert gas (nitrogen), together with only a slight excess of one or other of the reacting gases above the quantity required for complete combustion.

A possible explanation of the results is that the mode of combustion in such mixtures differs from that in mixtures containing a large excess of either of the reacting gases. Such an explanation is supported by the analyses of the "flame gases" recorded by Burgess and Wheeler in the paper to which reference has already been made. The samples of gas were rapidly snatched from the flames in such a manner as to cool the primary products of combustion before secondary reactions could come into play. It will be seen on examining the table of analyses (p. 2604) that all mixtures containing less than 15 per cent. of oxygen appear to be influenced by the deficiency of reacting gas (whether methane or oxygen), and it is in these mixtures that the generalisation regarding limiting percentages no longer holds. With the upper-limit mixtures of low oxygen content, the primary products of combustion contain smaller quantities of hydrogen than of carbon monoxide, whereas with the higher-limit mixtures containing a greater proportion of oxygen, the quantities of hydrogen and carbon monoxide produced are equal.

Similarly with the lower-limit mixtures of low oxygen content, the primary products of combustion contain more carbon monoxide than hydrogen, whilst with lower-limit mixtures containing more than 15 per cent. of oxygen these gases are absent altogether from the products of combustion. Further consideration of these results is reserved for a future communication, as is also the consideration of the displacement of the range for maximum speed of uniform movement of flame in mixtures of air with inflammable gases.

The Uniform Movement of Flame in Limit Mixtures.

The speed of horizontal propagation of flame in the limit mixtures in a tube 2.5 cm. in diameter was determined by the method described by Wheeler (T., 1914, 105, 2606). The results are given in table IV.

TABLE IV.

Speed of Propagation of Flame in Limit Mixtures of Methane, Oxygen, and Nitrogen in a Tube 2.5 cm. in Diameter.

Percentage of oxygen in atmos- phere.	Speed in cm. per sec.	
	Lower limit.	Upper limit.
13.7	21.9	19.1
17.0	22.4	19.0
21.0 (air)	23.3	19.1
33.0	23.0	18.9
50.0	22.8	18.9
66.0	21.3	19.4
100.0	19.9	18.9

The upper-limit speeds are identical within the range of experimental error. The speeds in the lower-limit mixtures are throughout slightly higher than the corresponding upper-limit speeds, although with pure oxygen the difference is very small. A noticeable feature of these flames, common to them all, was their small size in comparison with the diameter of the tube. This was more marked with the flames in the upper-limit than in the lower-limit mixtures, a fact which no doubt accounts for the slower speed of the former flames. For the smaller the flame, the greater is its surface in proportion to its volume, and the greater in proportion is the transference of heat from the flame to the walls of the tube. If this explanation be correct, it follows that the speeds of flames in limit mixtures should increase with increased diameter of the tube in which they travel. This was found to be so by Mason and Wheeler (T., 1917, 111, 1052).

With tubes of very small diameter, on the other hand, the speed of flame at the limits is comparatively high (Payman and Wheeler, T., 1918, 113, 656), but for another reason. With such tubes, the cooling effect of the walls is so great as to have a marked effect on the value of the limits, the range of inflammability of the mixtures rapidly narrowing as the diameter of the tube is diminished. Moreover, convection currents have no appreciable influence in tubes of such small diameter.

It seemed probable that the speed of flame in a limit mixture, determined under standard conditions, should approach a constant value irrespective of the nature of the inflammable gas. To test this, the speeds of flame have been determined in limit mixtures of air with several of the paraffin hydrocarbons. The results are given in table V, which is of value also in recording the limits of inflammability (horizontal propagation of flame).

The limits differ slightly from those found (central ignition in

a large globe) by Burgess and Wheeler, whose results are inserted in the table in brackets.

In the upper-limit mixtures the flames vibrated rapidly about half-way along the tube, and were sometimes extinguished there. The difference between a limit mixture and one which could only propagate flame for a short distance, if at all, was, however, well marked.

TABLE V.

Limits of Inflammability and Limiting Speeds of Flame in Mixtures of Air with the Paraffin Hydrocarbons in a Tube 2.5 cm. in Diameter.

Hydrocarbon.	Lower limit.		Upper limit.	
	Per cent. of combustible.	Speed, cm. per sec.	Per cent. of combustible.	Speed, cm. per sec.
Methane, CH_4	5.8 (5.6)	23.3	13.3 (14.8)	19.1
Ethane, C_2H_6	3.3 (3.4)	18.1	10.6 (10.7)	19.7
Propane, C_3H_8	2.4 (2.3)	20.8	7.3 (7.3)	20.3
Butane, C_4H_{10}	1.9 (1.6)	20.1	6.5 (5.7)	20.3
Pentane, C_5H_{12}	1.6 (1.4)	20.2	5.4 (4.5)	20.2
($\text{CH}_4 + \text{C}_5\text{H}_{12}$ *)	2.6 (2.5)†	22.3	7.7 (7.7)†	20.7

* Equimolecular mixture of methane and pentane.

† Calculated from values for methane and pentane.

The "limit speed" is thus found to approach a constant value, as foreshadowed by Burgess and Wheeler (T., 1914, 105, 2596), not only with each of the paraffin hydrocarbons singly, but also with the mixture of methane and pentane. There is no reason to doubt but that the limit speed of flame would have the same value for any mixture of the paraffins.

The speeds of flame in limit mixtures with air of carbon monoxide and hydrogen have also been determined. With carbon monoxide, the speed at both limits (in a tube 2.5 cm. in diameter) is 19.4 cm. per second, which agrees well with the speeds for the paraffins. With hydrogen, the speed at the lower limit is remarkably slow, namely, 10 cm. per second. The flame is exceedingly small, consisting of a tiny ball of flame, which, however, travels the full length of the tube. For reasons given in a previous communication (this vol., p. 41), it was not found possible to determine accurately the speed of flame in the upper-limit mixture of hydrogen and air.

The equimolecular mixture of methane and pentane corresponds with propane in percentage composition and calorific value, and yields the same products on complete combustion. The marked difference between the limits of inflammability of the mixed gases and those of propane shows that these are not the only factors on which the limits of inflammability depend. Similarly, a mixture

of three volumes of pentane and two volumes of hydrogen corresponds with propane, but this mixture of gases has limits 2.5 (lower) and 8.6 (upper) as compared with propane, 2.4 and 7.3.

These differences are perhaps due to the ability of the constituents of the mixed inflammable gases to burn independently. This subject will be dealt with more fully in succeeding papers of this series.

EXPERIMENTAL.

The speeds of propagation of flame in limit mixtures were determined in glass tubes by the method described by Wheeler (T., 1914, 105, 2610). Two tubes were employed, both 2.5 cm. in diameter; one, 3 metres long, used for the majority of the experiments; the other, used for the mixtures with atmospheres rich in oxygen, was only 1.5 metres long, so as to avoid the setting up of the detonation wave, with consequent shattering of the tube.

The platinum firing points were about 2 cm. from the open ends of the tubes. At measured distances along each tube were fused ground-glass tubulures, which carried glass plugs with stout platinum wires fused through them. Fine "screen wires" of copper were stretched across these platinum supports inside the tube, and electrical connexion was established with an automatic commutator and chronograph by means of platinum terminals on the outside of the plugs.

In order to fill the tubes with the mixture required for experiment, they were exhausted of air by means of an oil-pump, half filled with the mixture, and re-exhausted before being finally filled. A sample of the gas was then taken for analysis.

The limits of inflammability for upward and downward propagation of flame were determined in a similar tube 1.5 metres long, but without side-pieces.

The gases were prepared in the usual manner, the paraffin hydrocarbons being purified by repeated liquefaction and subsequent fractional distillation until, on explosion of a sample with excess of air and oxygen, the theoretical value for the ratio C/A was obtained.

The methane used in the limit determinations in pure oxygen contained 99.8 per cent. of CH_4 , and the ratio C/A was found to be 2.00. The oxygen was prepared by gently heating recrystallised potassium permanganate, and contained 99.6 per cent. of O_2 .

The gases were stored over water rendered alkaline by potassium hydroxide, and the mixtures were therefore saturated with water vapour.

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CXXXVI.—*The Propagation of Flame in Complex Gaseous Mixtures. Part II. The Uniform Movement of Flame in Mixtures of Air with the Paraffin Hydrocarbons.*

By WILLIAM PAYMAN.

IN the preceding paper it was shown that all mixtures of limit mixtures are themselves limit mixtures. With each of the paraffin hydrocarbons, the speed of the uniform movement of flame at the limits tends to a constant value under standard conditions of experiment. The same speed was found with all limit mixtures of methane, oxygen and nitrogen, and with an equimolecular mixture of methane and pentane at its limits with air. There is no reason to doubt that the same speed would be obtained with all mixtures of the paraffin hydrocarbons at the limits.

The generalisation advanced in the previous paper was thus shown to apply to all such mixtures. The question immediately arises whether what is true of the speeds of flames at the limits holds also for other speeds. Whether, for example, given two or more mixtures of air with different individual gases, in each of which the speed of flame was the same, all combinations of the mixtures would propagate flame at the same speed. Should this be so, a simple method would be available for the calculation of the speed of propagation of flame in complex gaseous mixtures from the known values for the simple constituent gases. Such a calculation could naturally only apply over the whole range of mixtures when the maximum speed of flame in mixtures of the several individual gases with air was the same; otherwise calculation would be restricted to such mixtures as possessed a speed of flame not greater than the lowest of the individual maximum speeds. It is clear, also, that the mixtures taken for the purpose of calculation must be all of the same nature; that is to say, must all contain excess of combustible gas, or must all contain excess of oxygen.

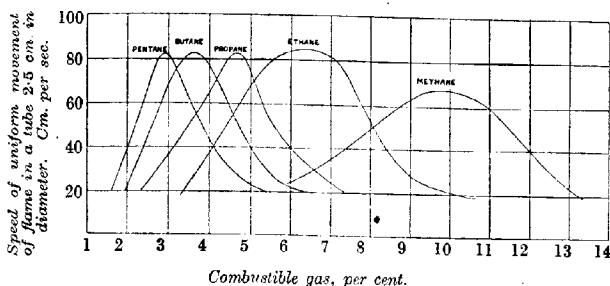
The mixtures of the paraffin hydrocarbons with air seemed most suitable to determine whether the generalisation that applies to speeds of flames at the limits is capable of extension to the speeds of the uniform movement over the whole range of inflammable mixtures.

Measurements were therefore made of the speed of the uniform movement in mixtures of air with each one of the hydrocarbons of the paraffin series up to and including pentane. The determinations were carried out as described in the previous paper, in a

horizontal glass tube 2.5 cm. in diameter and 3 metres long. The results are recorded in table I. The majority of the values in column 1 for methane were obtained by Mason and Wheeler (T., 1917, 111, 1052).

The results are shown diagrammatically in Fig. 1. With the exception of methane, the maximum speeds are approximately the same, namely, about 82 cm. per second. The value for methane is rather lower than this, being 67 cm. per second. Owing to the few data available for the thermal constants of the paraffin hydrocarbons, it is not easy to explain this difference. In each instance, the mixture having the maximum speed of flame contains more combustible gas than is required for complete combustion.

FIG. 1.



For testing the application of the generalisation * to speeds other than the limiting speeds, the gases methane and pentane were first chosen, since they were both readily obtainable in ample quantity. Two air mixtures were prepared, one containing 7.35 per cent. of methane and the other 1.98 per cent. of pentane. In these two mixtures the speed of the uniform movement is the same, about 40 cm. per second (twice the speed at the limits), and they both contain excess of oxygen. The mixtures were then combined in varying proportions, and the speeds of the uniform movement determined in the usual manner. The results are recorded in table II.

* This may be termed the "speed generalisation."

TABLE II.

Speeds of Uniform Movement of Flame in a Glass Tube 2.5 cm. in Diameter with Mixtures containing 7.35 per cent. of Methane and 1.98 per cent. of Pentane, respectively, Mixed Together.

Methane mixture. Per cent.	Pentane mixture. Per cent.	Speed, cm. per sec.
100.0	—	39.3
75.0	25.0	39.2
50.0	50.0	39.6
25.0	75.0	39.9
21.2	78.8	39.2*
—	100.0	40.1

* Methane and pentane in equimolecular proportions.

It will be seen that the speeds are identical within the limits of experimental error.

Two mixtures containing excess of combustible gas, with speeds further removed from that at the limits, were then examined in the same manner. These mixtures contained 11.00 per cent. of methane and 3.54 per cent. of pentane, respectively, and the speed of the uniform movement of flame in them was about 60 cm. per second, three times the value at the limits. The results are given in table III.

TABLE III.

Speeds of Uniform Movement of Flame in a Glass Tube 2.5 cm. in Diameter with Mixtures containing 11.00 per cent. of Methane and 3.54 per cent. of Pentane, respectively, Mixed Together.

Methane mixture. Per cent.	Pentane mixture. Per cent.	Speed, cm. per sec.
100.0	—	59.1
75.0	25.0	59.1
50.0	50.0	60.3
25.0	75.0	59.1
24.4	75.6	59.1*
—	100.0	59.6

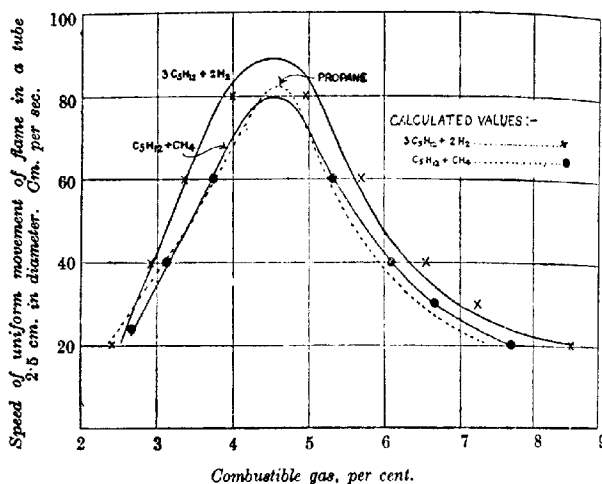
* Methane and pentane in equimolecular proportions.

Once more the generalisation is found to hold with great accuracy, and there is no doubt that it is true for all mixtures of the paraffins having the same speeds of flame provided that the maximum speed in mixtures of any individual paraffin with air is not too nearly approached. For if the generalisation could be supposed to apply to the "maximum-speed" mixtures, no mixture of air containing both methane and pentane should propagate the

uniform movement of flame at a speed higher than the maximum speed in mixtures of methane and air. Similarly, the generalisation cannot apply to speeds at the limits in mixtures of methane with atmospheres containing a high proportion of nitrogen, for with such atmospheres both upper and lower limits of inflammability lie at the maximum, flattened portion of the speed-percentage curve.

Bearing these limitations in mind, it should be possible to calculate the values for the speed-percentage curve for any combination of the paraffins in air. An equimolecular mixture of methane and

FIG. 2.



pentane (which corresponds with propane) was chosen to test the accuracy of such calculations.

The results are recorded in table IV, and are compared with the calculated values in Fig. 2. In no instance was the difference between observed and calculated speeds greater than 1 cm. per second. The highest speed for which calculation was made was 60 cm. per second.

It must be admitted that the gases chosen for these experiments are particularly favourable towards the calculation, since the maximum speed of the uniform movement is nearly the same with each gas. As a more stringent test, a mixture of pentane and hydrogen was prepared ($3C_5H_{12} + 2H_2$, corresponding with propane), and a

series of speed determinations and calculations made as before. In this instance, the maximum speeds of uniform movement in mixtures of the individual gases with air differ widely, being 82 cm. per second for pentane and 485 cm. per second for hydrogen. The results are recorded in table IV, and in Fig. 2 are compared with those calculated.

TABLE IV.

Speed of Uniform Movement of Flame in Mixtures of Air with Combinations of Gases corresponding with Propane in a Glass Tube 2.5 cm. in Diameter.

(a) $\text{CH}_4 + \text{C}_5\text{H}_{12}$		(b) $3\text{C}_2\text{H}_6 + 2\text{H}_2$	
Combustible gas.	Speed,	Combustible gas.	Speed,
Per cent.	cm. per sec.	Per cent.	cm. per sec.
2.55	6 cm. travel only	2.35	Cap only
2.65	22.3	2.47	19.7
3.12	39.2	3.02	43.3
3.54	53.7	3.56	67.7
4.04	70.7	4.03	82.7
4.52	78.3	4.48	89.5
5.05	73.6	4.91	83.7
5.36	59.1	5.77	54.0
6.23	37.5	6.25	43.6
7.03	25.4	7.10	27.9
7.70	20.7	7.80	23.1
7.79	3 cm. travel only	8.60	21.5
		8.72	15 cm. travel

The results are not in as good agreement with calculation as those obtained with the combination of methane and pentane, but, even so, the agreement is remarkably close considering the wide difference between the individual maximum speeds of flames. The greatest difference between observed and calculated results is only 4 cm. per second. The highest speed for which calculation was made was 60 cm. per second, which is rather close to the maximum speed for pentane.

It will no doubt be apparent that a limit is at present set to the scope of the generalisation, because only the speeds of flames in mixtures with air are available for purposes of calculation. When it is remembered that the gas with the slower maximum speed of uniform movement of flame may have that maximum greatly enhanced if an atmosphere richer in oxygen than air is used, it is clear that the generalisation should be capable of further extension, given the necessary experimental data. The consideration of this subject is reserved for a later paper.

It now remains to deduce a method for calculating the maximum speed of the uniform movement of flame in a mixture of air with a mixture of inflammable gases, and also for calculating the com-

position of the mixture which will have this maximum speed of flame. The latter may be calculated by the method suggested in a previous communication (Payman and Wheeler, this vol., p. 36), in which it was shown that if "maximum-speed" mixtures were mixed together, the result would be the "maximum-speed" mixture for the mixed inflammable gases. For example, the value for the maximum speed of uniform movement of flame for hydrogen is 38.5 per cent., for pentane 2.9 per cent., and for methane 9.9 per cent.* The calculated value for the equimolecular methane-pentane mixture is 4.48 per cent., and for the pentane-hydrogen mixture ($3C_5H_{12} + 2H_2$) 4.60 per cent. The value found is the same for both mixtures, namely, 4.55 per cent. It is interesting to note that the same value is found for propane, with which these mixed inflammable gases correspond.

It was also suggested, from a consideration of the results obtained with mixtures of air with an equimolecular mixture of methane and hydrogen, that the gas for which the maximum speed of flame was the lower had the predominating effect in determining what would be the maximum speed with mixed inflammable gases. This is true for mixtures of methane and hydrogen, but, in general, it is the gas requiring most air to attain the maximum speed of flame which is the deciding factor. This is, indeed, what one would expect from a consideration of the generalisation concerning the speeds in mixed gases. The larger the volume of air a combustible gas requires to produce its "maximum-speed mixture," the smaller is the percentage of that combustible gas in the fastest-speed mixture of air with a mixture of gases that contain it.

A method for calculating approximately the maximum speed of the uniform movement of flame in mixtures of air with a mixed inflammable gas, from the known values for its simple constituents, may be given from a consideration of this fact. The assumption is made that when "maximum-speed" mixtures are mixed together, the resulting speed is proportional to the amount of each mixture present and to the respective maximum speeds of their flames. This relationship, which holds roughly for mixtures with air, may be expressed as follows:

$$S = \frac{aS_a + bS_b + cS_c + \dots}{a + b + c + \dots},$$

where S is the speed required; a, b, c, \dots are the amounts present of each maximum-speed mixture with air; S_a, S_b, S_c, \dots are the speeds of flame in those mixtures respectively.

The use of the formula will be best explained by an actual

* In each instance the figure given is the mean percentage over a range of mixtures having nearly the same speed.

calculation of the maximum speed of flame for the equimolecular mixture of methane and pentane in admixture with air.

The calculated value for the mixture to have the maximum speed of flame is 4.5 per cent., and this mixture will contain 2.25 per cent. each of methane and pentane. In the maximum-speed mixture of pentane and air, 100 parts of the mixture contain 2.9 parts of pentane, and therefore 2.25 parts of pentane correspond with $\frac{2.25}{2.9} \times 100 = 77$ parts of pentane-air mixture.

Similarly, 2.25 parts of methane correspond with 23 parts of methane-air mixture, since the maximum-speed mixture of methane and air contains 9.9 per cent. of methane.

Substituting these values in the above formula,

$$S = \frac{(77 \times 82) + (23 \times 67)}{100} \\ = 78.5 \text{ cm. per second.}$$

The value found was 79 cm. per second, showing an extremely close agreement.

The agreement is not so good with the pentane-hydrogen mixture ($3C_5H_{12} + 2H_2$), the calculated value being 100 cm. per second and the speed found 90 cm. per second. The discrepancy does not appear so great, however, when it is remembered that there is a difference of 400 cm. per second between the maximum speeds of the flames in mixtures of pentane and air and hydrogen and air.

The maximum speed of flame with mixed gases and air may also be found by a graphical method. If on a speed-percentage graph the maxima for any two gases taken singly is joined by a straight line, all the maxima for mixtures of these two gases lie approximately on this line. The composition of the "maximum-speed" mixture is calculated by the method given by Payman and Wheeler (*loc. cit.*), and the speed then read off from the graph.

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CXXXVII.—*The Propagation of Flame in Complex Gaseous Mixtures. Part III. The Uniform Movement of Flame in Mixtures of Air with Mixtures of Methane, Hydrogen and Carbon Monoxide, and with Industrial Inflammable Gases.*

By WILLIAM PAYMAN.

THE common industrial gases contain as their inflammable constituents methane, hydrogen, and carbon monoxide in various proportions.

The speed of the uniform movement of flame in mixtures of methane and air in a tube 2.5 cm. in diameter was given in Part II of this series of papers. The speeds with hydrogen and air in a similar tube (over the major portion of the range of inflammable mixtures) have been determined by Haward and Otagawa (T., 1916, 109, 83). The speeds in mixtures of carbon monoxide and air are recorded in the present paper.

Mixtures of Carbon Monoxide and Air.—It is well known that the rate of combustion of carbon monoxide is dependent on the amount of water vapour present. Dixon, for example (*Phil. Trans.*, 1893, 184, 97), has shown that the velocity of the detonation wave in a mixture of carbon monoxide and oxygen ($2\text{CO} + \text{O}_2$) increases with the percentage saturation of water vapour.

The present series of determinations of the speed of the uniform movement of flame in mixtures of carbon monoxide and air was carried out with mixtures saturated with water vapour at the ordinary temperature and pressure. Since the room temperature varied, it was not surprising to find that the speed in a given mixture did not remain constant from day to day. Identical results were, however, obtained in experiments made within a few minutes of each other at the same temperature and pressure. Table I illustrates the effect of change in the percentage saturation of water vapour on the speed of the uniform movement of flame in a mixture of carbon monoxide and air containing 50 per cent. of carbon monoxide.

TABLE I.

Speed of Uniform Movement of Flame in a Mixture of Carbon Monoxide and Air (50 per cent. CO) in a Tube 2.5 cm. in Diameter.

Temperature and pressure.	Cm. per sec.	
10° and 750 mm.	(1) 59.9	(2) 59.9
15° and 750 mm.	(1) 65.0	(2) 64.5
17° and 755 mm.	(1) 79.4	(2) 79.0

A series of determinations of speeds of flame over the whole range of inflammable mixtures was carried out during a period when the temperature of the laboratory did not alter appreciably (about 12°). The values obtained are given in table II.

TABLE II.

Speed of Uniform Movement of Flame in Mixtures of Carbon Monoxide and Air in a Tube 2.5 cm. in Diameter at 12° and 750 mm.

Per cent. of carbon monoxide.	Cm. per sec.	Per cent. of carbon monoxide.	Cm. per sec.
16-15	Tongue of flame only.	59-81	54-2
16-29	19-5	65-55	37-4
16-40	19-4	65-84	36-3
16-51	19-4	67-10	30-2
24-47	34-0	67-57	29-6
30-50	46-0	69-00	26-0
44-84	60-1	70-63	20-0
50-45	59-9	70-68	20-3
54-40	57-8	71-19	19-4
59-58	56-2	71-31	Trailing flame travelled 15 cm.

These values are of interest in themselves, apart from their connexion with the problem of the propagation of flame in complex gaseous mixtures, inasmuch as they disclose the fact that the maximum speed of flame is obtained with mixtures containing from 45 to 50 per cent. of carbon monoxide. The mixture for complete combustion contains 29.5 per cent. carbon monoxide, so that the "displacement" of the maximum-speed mixture is greater even than with hydrogen, despite the fact that the thermal conductivity of carbon monoxide is but little different from that of air.

Industrial gas mixtures may contain varying proportions of water vapour. There may therefore be some uncertainty as to the correct values to use for the speed of flame in mixtures of carbon monoxide and air when attempting to calculate the speed of flame in the mixed industrial gas. Such gases, however, contain hydrogen as well as carbon monoxide, and the presence of hydrogen affects the speed of flame in a similar degree to that of water vapour. With mixtures of gases containing fairly high proportions of hydrogen, it is therefore not unlikely that the effect of variation in the moisture content would be inappreciable. It should therefore be sufficient for our purpose to know the values for the speed of flame in mixtures of air with a mixture of hydrogen and carbon monoxide. Or the "effective" speeds for mixtures of carbon monoxide and air could be calculated from such values and these speeds used for further calculation.

In this connexion, it is interesting to note that Berthelot (*Ann. Chim. Phys.*, 1881, [v], 28, 289) found the rate of detonation in mixtures of carbon monoxide and oxygen to be about half the calculated value. For mixtures of oxygen with carbon monoxide plus hydrogen, the calculated values were in good agreement with those found. Similarly, in the present research, the maximum speed of uniform movement of flame in mixtures of carbon monoxide and air is found to be about half the value calculated, making use of the values determined for hydrogen-air and hydrogen-carbon monoxide-air mixtures.

Mixtures of Hydrogen and Air.—As with tubes of smaller diameter (this vol., p. 36), it was not found possible to determine accurately the speed of the uniform movement of flame in the upper-limit mixture of hydrogen and air in a tube 2.5 cm. in diameter. A mixture containing 71.4 per cent. of hydrogen was found to be the richest which would propagate flame under the experimental conditions. The flame was not hot enough to melt "screen wires," but its speed, as measured by means of a tapping key in connexion with a chronograph, was found to be approximately 50 cm. per second.

A characteristic of the lower-limit mixture and of mixtures near to it is the formation on ignition of minute balls of flame, which pass steadily from the open to the closed end of the tube. These flames are propagated mainly by the influence of convection currents, and the speed-percentage curve at the lower-limit region is not continuous, but shows a definite break. Nevertheless, no definite distinction, at the point of break in the curve, could be drawn between the normal and the balls of flame, the latter increasing in size and gradually changing their form as the percentage of hydrogen increased.

The speeds of the flames in mixtures near the limits are given in table III, which completes the table given by Haward and

TABLE III.

Speed of the Uniform Movement of Flame in Mixtures of Hydrogen and Air in a Tube 2.5 cm. in Diameter.

Hydrogen. Per cent.	Speed, cm. per sec.
6.10	No flame observed.
6.19	10
6.31	12
6.52	15
14.71	120
71.39	50
71.51	Flame to open end only.

Otagawa (*loc. cit.*, p. 89). In only one instance was the flame hot enough to melt "screen wires," namely, with the mixture containing 14.71 per cent. of hydrogen; the remaining speeds were determined by means of a tapping key.

Mixtures of Methane, Hydrogen, and Air.—The speed of the uniform movement of flame in a tube 2.5 cm. in diameter was determined over a range of mixtures of air with two mixtures of methane and hydrogen. The first mixture contained equal volumes of methane and hydrogen ($\text{CH}_4 + \text{H}_2$), the second three volumes of methane to one volume of hydrogen ($3\text{CH}_4 + \text{H}_2$). The results are recorded in table IV. The lower-limit flames preserved the general character of the corresponding hydrogen flames, and their speeds were found to be lower than the speed in the limit mixture of methane and air.

TABLE IV.

Speed of the Uniform Movement of Flame in Mixtures of Air with Hydrogen Methane Mixtures in a Tube 2.5 cm. in Diameter.

$\text{CH}_4 + \text{H}_2$		$3\text{CH}_4 + \text{H}_2$	
Combustible gas. Per cent.	Speed, cm. per sec.	Combustible gas. Per cent.	Speed, cm. per sec.
6.03	15.0	6.09	18.0
6.20	17.1	6.22	19.9
6.31	19.1	6.50	21.0
6.73	22.1	6.80	27.7
7.68	28.6	7.84	39.6
9.05	45.6	9.06	58.3
10.23	67.4	9.93	78.7
11.95	104.1	11.35	84.9
11.99	106.3	12.26	82.2
13.50	128.6	13.25	66.7
14.93	135.3	14.20	45.7
15.93	127.3	14.99	27.8
16.90	111.9	15.50	22.6
18.31	65.6		
19.96	35.5		
20.22	30.5		
20.32	28.5		
20.48	27.3		
20.80	24.3		

The results are plotted as curves in Fig. 1, the calculated curves being shown in dotted line. The maximum speeds calculated by the method given in Part II are 150 and 99 cm. per second respectively for the mixtures $\text{CH}_4 + \text{H}_2$ and $3\text{CH}_4 + \text{H}_2$. The values found were 135 and 85 cm. per second.

Mixtures of Carbon Monoxide, Hydrogen, and Air.—Two mixtures of carbon monoxide and hydrogen were employed, of composition $\text{CO} + \text{H}_2$ and $3\text{CO} + \text{H}_2$, corresponding with the methane-hydrogen mixtures. The results are given in table V, and are plotted as curves in Fig. 2.

FIG. 1.

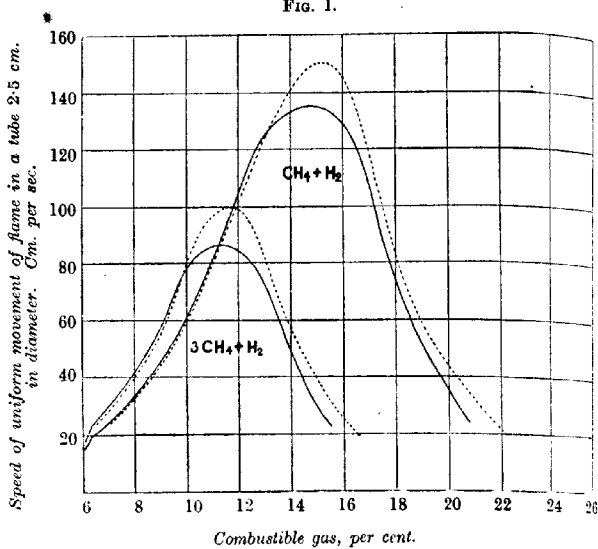
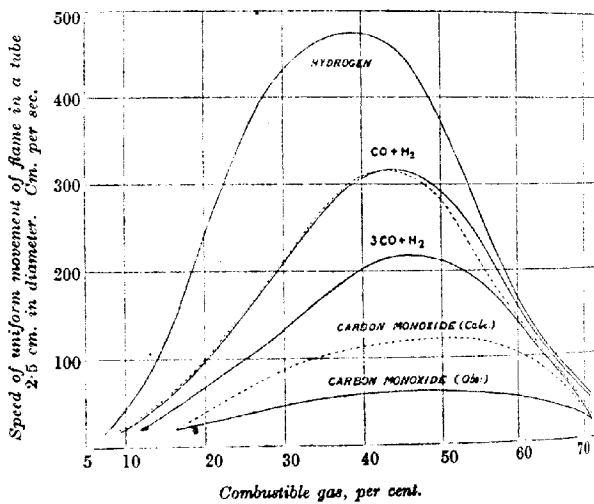


FIG. 2.



From the values found for hydrogen and for the mixture $3\text{CO} + \text{H}_2$, the speeds of the flames in mixtures of air with $\text{CO} + \text{H}_2$ were calculated. The results are shown in dotted line in Fig. 2. The values for carbon monoxide and air were also calculated from these values, and the curve is given in the diagram for comparison. It will be seen that the values calculated in this manner are much higher than those found by experiment. These "effective" speeds have been used in subsequent calculations instead of the values as determined, which are dependent on the amount of water vapour present.

TABLE V.

Speed of Uniform Movement of Flame in Mixtures of Air with the Mixtures $\text{CO} + \text{H}_2$ and $3\text{CO} + \text{H}_2$ in a Tube 2.5 cm. in Diameter.

$\text{CO} + \text{H}_2$.		$3\text{CO} + \text{H}_2$.	
Combustible gas.	Speed,	Combustible gas.	Speed,
Per cent.	cm. per sec.	Per cent.	cm. per sec.
9.25	18.2	12.00	19.2
10.35	21.1	18.99	67.1
15.40	58.3	27.82	115.0
20.57	100.4	34.73	166.2
30.25	211.5	41.32	205.5
36.94	282.9	46.90	214.0
41.50	309.7	53.17	200.0
45.92	315.2	58.49	154.7
51.23	280.0	70.36	34.4
58.55	178.5	71.42	20.8
69.00	64.5		
70.75	50.1		
71.34	44.4		

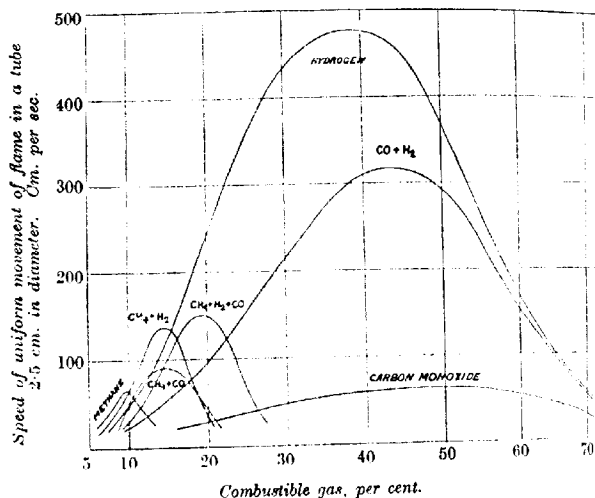
Mixtures of Methane and Carbon Monoxide, and Mixtures of Methane, Hydrogen, and Carbon Monoxide with Air.—Table VI records the results obtained with a mixture containing equal volumes of methane and carbon monoxide, and with one containing equal volumes of methane, hydrogen, and carbon monoxide. Methane, or any gas into the composition of which hydrogen enters, acts towards mixtures of carbon monoxide and air in a manner comparable with that of hydrogen and water vapour. The maximum speed of uniform movement of flame in mixtures of air with each of the mixtures $\text{CH}_4 + \text{CO}$ and $\text{CH}_4 + \text{CO} + \text{H}_2$ was found to be 91 and 150 cm. per second respectively, whilst the corresponding calculated values are 78 and 145 cm. per second.

TABLE VI.

Speed of Uniform Movement of Flame in Mixtures of Air with the Mixtures $\text{CH}_4 + \text{CO}$ and $\text{CH}_4 + \text{H}_2 + \text{CO}$ in a Tube 2.5 cm. in Diameter.

$\text{CH}_4 + \text{CO}$.		$\text{CH}_4 + \text{H}_2 + \text{CO}$.	
Combustible gas, Per cent.	Speed, cm. per sec.	Combustible gas, Per cent.	Speed, cm. per sec.
9.45	21.9	7.70	21.2
9.88	36.2	10.01	36.5
12.07	62.5	14.01	83.3
13.73	85.7	15.80	109.4
15.95	91.3	18.92	150.0
18.06	68.9	20.42	148.7
19.32	52.3	22.43	118.5
21.55†	19.8	25.05	57.8
		27.57	21.8

FIG. 3.



The speed-percentage curves for the equimolecular mixtures $\text{CH}_4 + \text{H}_2$, $\text{H}_2 + \text{CO}$, $\text{CO} + \text{CH}_4$, and $\text{CH}_4 + \text{H}_2 + \text{CO}$ are plotted in Fig. 3, the curves for the pure gases being included for comparison.

Mixtures of Industrial Gases with Air.—The equimolecular mixture of carbon monoxide and hydrogen correspond nearly with "water-gas." A coal-gas and a producer-gas were also examined, the compositions of these being:

	Coal-gas. Per cent.	Producer-gas. Per cent.
Benzene and higher olefines	1.1	—
Carbon dioxide	0.3	5.0
Ethylene	2.6	—
Carbon monoxide	9.6	21.3
Hydrogen	49.2	12.6
Methane and higher paraffins	33.9	3.1
Nitrogen (by difference)	3.3	58.0

The speeds of the uniform movement of flame in mixtures of air with each of these two gases are given in table VII.

TABLE VII.

Speed of Uniform Movement of Flame in Mixtures of Air with Coal-gas and with Producer-gas in a Tube 2.5 cm. in Diameter.

Coal-gas. Per cent.	Speed, cm. per sec.	Producer-gas. Per cent.	Speed, cm. per sec.
7.2	21.5	24.7	20.0
10.0	50.5	38.9	47.4
11.9	87.1	46.0	62.7
14.7	133.7	49.0	72.2
16.8	153.9	54.3	69.7
17.9	154.1	58.8	43.5
20.4	115.6	61.6	24.0
21.8	74.3		
24.3	22.0		

The principal constituents of the coal-gas are hydrogen, methane, and carbon monoxide. If all the hydrocarbons be reckoned as methane, the calculated maximum speed of uniform movement of flame in mixtures of air with this coal-gas is 164 cm. per second, with a mixture containing 18.4 per cent. of coal-gas. Since the content of inert gases (nitrogen and carbon dioxide) is low, they may be neglected when making the calculations.

Producer-gas, on the other hand, always contains a large proportion of inert gas; the sample used for these experiments contained only 37 per cent. of combustible gas. For this reason, a value for the maximum speed of uniform movement of flame in a mixture of producer-gas and air, calculated from the maximum speeds in mixtures of the pure gases with air, would be too high.

The speed of flame in mixtures of air with gas containing a large proportion of nitrogen can be calculated on the assumption that the cooling or retarding effect on the flame of excess of air or of nitrogen will be the same, since their specific heats are the same.* A mixture of carbon monoxide, hydrogen, and methane in the pro-

* This assumption is not quite correct, since the presence of reactive gas slightly opposes the retarding effect of air.

portions in which they are found in the sample of producer-gas used in these experiments will have as its "fastest-speed" mixture with air one containing 34.7 per cent. of combustible gases. If nitrogen is added to this mixture, so that the ratio of nitrogen to combustible gases is the same as in the producer-gas, the result is a mixture containing 21.7 per cent. of combustible gases. (The carbon dioxide content being low, it may be calculated as nitrogen.) The speed of flame in this mixture should, on the assumption given above, be but little different from the speed of flame in the same mixture of combustible gases with air. The latter speed is most easily determined by a graphical method, and is found to be 85 cm. per second.

The mixture of air and producer-gas with the fastest speed of uniform movement of flame contains slightly more inflammable gases than is required for complete combustion. A greater "displacement" of the maximum-speed mixture might be expected for the reason that the chief inflammable constituents are hydrogen and carbon monoxide, the individual displacements of which are considerable. The small displacement with producer-gas is due to the presence of inert gases, as will be explained in the succeeding section of this series of researches. The effect, in general, of inert gases on the speed of the uniform movement of flame in gaseous mixtures will also be considered.

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CUMBERLAND.

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CXXXVIII.—*The Ignition of Ether-Alcohol-Air and Acetone-Air Mixtures in Contact with Heated Surfaces.*

By ALBERT GREVILLE WHITE and TUDOR WILLIAMS PRICE.

Owing to the large number of fires which had occurred during 1917 and 1918 in solvent-recovery stoves in which cordite was being dried, it was decided to investigate the conditions under which mixtures of the vapours of ether, alcohol, and acetone with air would ignite. This was rendered all the more necessary by the fact that the information available on this subject was scanty and often contradictory.

As a general rule, the actual rise in temperature necessary to cause the explosion of such an explosive as glyceryl trinitrate is much lower than that needed to ignite an explosive gaseous mix-

ture. On the other hand, the lower thermal capacity of the gas and its comparatively far greater mobility render it more susceptible to ignition in many cases. There was thus some justification for the idea that the solvent-air mixture was probably responsible for many of the recovery-stove fires that had occurred, particularly when it is remembered that fires had been less frequent in "final" stoves than in recovery-stoves, that more fires had occurred with cordite from which a mixture of ether and alcohol was being removed than when the solvent was acetone, and that ether when mixed with air is indubitably more dangerous than acetone under similar conditions.

The factors affecting the ignition of a combustible gaseous mixture are many, and the influence of some of them is not particularly well understood. The problem of safety when dealing with such a mixture under manufacturing conditions divides itself naturally into two parts, the one dealing with the ignition of the mixture, and the other with the propagation of the flame from one portion of the mixture to another, for example, from one building to another. This division is seen to be inherent when it is remembered that, by using a sufficiently powerful source of ignition, it is possible to ignite almost any combustible gas-air mixture, whereas the propagation of the flame is a totally different matter, particularly if the gas-mixture considered is at rest. In such a case, there appear to be definite limits for the proportion of combustible gas to air in a mixture which propagates flame, these limits depending ultimately only on the direction of propagation and the nature of the combustible gas used, at ordinary temperature and pressure. The experimental work is accordingly divided into three sections:

- (1) The ignition-temperatures of various gas-mixtures, including ether-air, alcohol-air, and acetone-air mixtures.
- (2) The limits for the propagation of flame in these mixtures.
- (3) The investigation of a few miscellaneous facts concerned more particularly with various means of ignition.

The fact has not been lost sight of that ease of ignition and propagation of flame might be enhanced by the presence of some impurity in the solvent vapour-air mixture. Accordingly, experiments have been carried out to ascertain the effect of adding slight amounts of glyceryl trinitrate and of the peroxides of ether to the gas-mixtures dealt with. This was the more necessary, as glyceryl trinitrate, even though present in the stove vapours in minute quantities, is known to be a source of possible danger, and also because there appears to be a tendency to assign any otherwise inexplicable explosion or fire with ether to the influence of these

peroxides (compare Neander, *Chem. Zeit.*, 1902, **26**, 336, and others). This idea seems to have arisen chiefly from the fact that ether which had given trouble had generally been kept for some time, and also because it was well known that the exposure of purified ether to light caused the formation of compounds which appeared to contain active oxygen. The methods used to prepare these compounds were those given by Baeyer and Villiger (*Ber.*, 1900, **33**, 3387; 1901, **34**, 738). Naturally, great care was exercised in freeing the solvents used from such impurities.

The ether used was twice distilled from acid permanganate and washed several times, first with a concentrated solution of potassium hydroxide in water, and then with a dilute one. It was then washed several times with distilled water, dried, distilled, and again dried for several days over sodium. On fractionating twice with a Young and Thomas still-head, a fraction boiling within 0.05° of the boiling point of the pure substance was collected each time. The alcohol used was ordinary absolute alcohol, which was twice heated under reflux for four hours over fresh lime, then twice over calcium turnings for two hours, and refractionated as for ether, the fraction collected boiling within 0.05° of 78.4° . The acetone was purified by converting it into the sodium iodide compound, collecting, and distilling the double compound. The product was then carefully dried and fractionated twice, as in the case of the other compounds. The purity of the solvents used can be gauged from the fact that the acetone obtained had D_4^{20} 0.7808, as low a figure as any published. These solvents were carefully preserved in a dark cupboard.

Except when otherwise specified, percentages can be taken to mean percentage by volume. Tubes are also often specified by their diameters. Thus a tube 5 cm. in diameter would be referred to as a 5 cm. tube.

SECTION I.

The Ignition-temperatures of Ether-Alcohol-Air and Acetone-Air Mixtures.

With the exception of two figures for ether in air, 1033° , given by McDavid (*T.*, 1917, **111**, 1003) and 190° by Alilaire (*Compt. rend.*, 1919, **168**, 729), the ignition-temperatures found in the literature for the solvents in question are spontaneous ignition-temperatures, which can be taken to be the temperatures at which the substances dealt with (surrounded by oxygen or air at the same temperature) will burst into flame without the application of any spark or other local high temperature. Two sets of these figures, which are intended for engine work, are given. Thus, Holm

(*Zeitsch. angew. Chem.*, 1913, **26**, i, 273) gives the spontaneous ignition-temperature of alcohol in air as 510° , of acetone as 570° , and of ether as 400° . Moore (*J. Soc. Chem. Ind.*, 1917, **36**, 109) gives the spontaneous ignition-temperatures of ether and alcohol in air as 347° and 518° , and in oxygen as 190° and 395° respectively. It will be seen that only the figure given for the ignition-temperature of ether in air by Alilaire, which was published after the completion of our work, appears to be sufficiently low to make an ignition of the solvent-air mixture under present-day conditions of recovery seem feasible.

A paper by Perkin (T., 1882, **41**, 363) on the luminous, incomplete combustion of ether is interesting in this connexion. According to him, this phenomenon was first discovered by Davy, who noticed a pale phosphorescent light round a hot platinum wire. Doebereiner noticed the same thing, and also remarked that when ether was dropped into a retort heated on the sand-bath to 100° and upwards, or into a platinum capsule exposed to the vapour of boiling water, the spheroidal state is produced, accompanied by a blue flame visible only in the dark, and not capable of setting fire to other substances, lachrymatory vapours of lampic acid being formed.

Boutigny and Miller also noted this flame and the products of the combustion, and proved that metal or porcelain dishes were equally effective in producing these phenomena. Boutigny gives the temperature at which ether begins to burn with this flame as a little below that of fusing lead, and so agrees with Perkin and others that the temperature necessary must be about 260° . As will be seen later, however, a temperature much below this is sufficient to produce this flame in ether-air mixtures. According to Perkin, this blue flame has a comparatively low temperature (it has since been designated a "cool" flame). The fingers may be placed in it with impunity. It will neither char paper nor ignite carbon disulphide, and a lucifer match may be held in it for some time before being ignited. He also states, however, that ether vapour burning with this blue flame, when in large quantities, or more especially in a confined space, rapidly increases in temperature and quickly enters into ordinary combustion.

Perkin also examined other substances for "the luminous appearance accompanying incomplete combustion." Only traces of blue flame were obtained with the alcohols up to amyl, methyl alcohol giving none.

The generally accepted definition of ignition-temperature is that temperature to which a gas-mixture must be heated, at least locally, for the speed of the reaction to be such as to become self-support-

ing. This temperature is not that at which a flame appears, but that at which self-heating becomes sufficient to cause ultimate inflammation.

That the determination of an ignition-temperature is a matter of great difficulty can at once be seen when it is considered that the temperature at which such a reaction would become self-supporting must depend on the rate of dissipation of heat in the system as well as on many other factors. For instance, if the time taken to bring the gas-mixture up to the ignition-temperature is appreciable, the composition of the gas-mixture alters, and if a solid is in contact with the heated gases, even below their ignition-temperature, as proved by Bone and Wheeler (*Phil. Trans.*, 1906, [A], 206, 1) and by Meyer and Freyer (*Ber.*, 1892, 25, 622), the most divergent results are obtained for the amount of combination that takes place. From their work, the German investigators concluded that it was impossible to determine an ignition-temperature.

We decided to try the soap-bubble method described by McDavid (*loc. cit.*), and if that proved unsatisfactory, as was anticipated from Meunier's work (*Compt. rend.*, 1907—1912), to attempt to make use of a method in which the amount of heated surface brought into contact with the gas would be known, thereby eliminating the most obvious defect in the soap-bubble method as published. To this end, it was decided to pass the various gas-mixtures of which the ignition-temperatures were required into certain uniformly heated vessels. In this way, the temperature at which ignition could be obtained in each vessel would be known. By taking vessels of the same material having different ratios of surface to volume and plotting the ignition-temperature against surface per unit volume, it was anticipated that by extrapolation it would be possible to eliminate to a great extent disturbing variations due to surface action. The most obvious vessels to use were tubes of various diameters, and a series of these was accordingly chosen. It was quite realised that the longer time taken to heat a large bulk of gas would affect the results to some extent, but direct experiment, in which some of the products of combustion were introduced into the gas-mixture to be used, soon proved this to be almost negligible in the case of ether-air mixtures of ordinary concentration. It is to be noticed, however, that in this method the temperature determined has been called the sub-ignition-temperature—the minimum temperature at which combination in a gas-mixture becomes self-supporting. This appears to be the practical temperature required, as the phenomenon obtained may or may not give rise to ordinary combustion, depending on circum-

stances. Its identity with the ignition-temperature of a mixture depends entirely on what is understood by "ignition," and a "flame" in those cases in which cool flames are possible phenomena.

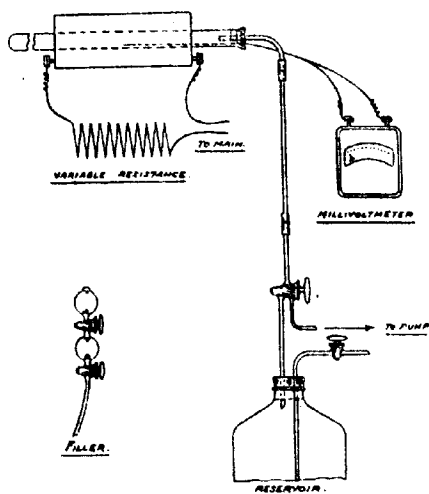
Heating a gas-mixture quickly to its ignition-temperature is always assumed to cause ultimate inflammation. In many cases, an ordinary flame, causing more or less complete combustion, cannot be obtained by heating a gas to its sub-ignition-temperature, and in those cases in which such a flame appears it is only produced through the "cool" flame of incomplete combustion. For a fairly concentrated ether-air mixture, the cool flame obtained is very similar in appearance to an ordinary flame, but for very dilute mixtures it becomes practically a travelling phosphorescent flow.

The Soap-bubble Method.—The results obtained during our investigation of the soap-bubble method of determining ignition-temperatures have already been published (this vol., p. 1248). By using different igniting surfaces, it was found that the ignition-temperature of a 5 per cent. ether-air mixture as determined by this method could vary from 907° to 1064° , whilst that of a 12 per cent. mixture could vary from 870° to 1035° . The results obtained seemed to be erroneous, and by using several gas-mixtures it was shown that the method could scarcely be trusted, even for comparative results.

The Exhausted Tube Method.—The apparatus used in this method is shown in Fig. 1. The heated vessel consisted of a long glass tube sealed at one end and closed at the other by means of a rubber stopper. The tube could be kept at any desired temperature by means of an electric furnace, the exact temperature inside the tube being registered by means of a copper-constantan couple except when that temperature was more than 500° , when a nitrogen-filled mercury thermometer was used. The ignition tube was connected to the glass reservoir containing the mixture under examination by means of a glass lead passing through the rubber stopper. A three-way tap was inserted between the tube and reservoir in such a manner that the tube and lead could be connected at will to the reservoir or to a Gaede box pump. The reservoirs were of 15 to 17 litres capacity, and the tubes used at first were a few cm. longer than the furnace, which was 50 cm. long. The reservoir was filled with any required mixture by exhausting it and allowing air to sweep a known weight of the solvent from the filler, shown in the figure. The filler was connected to the three-way cock by means of rubber tubing, but the end of the filler always projected into the tap tube. In this way, none of the solvent escaped introduction into the reservoir, and a knowledge of the molecular weight of the solvent, together with

the temperature and pressure, gave, by means of a simple calculation, the percentage volume occupied by the solvent in the reservoir. A portion of the lead between the three-way tap and the furnace was connected to the remainder by means of rubber joints. These joints enabled tubes of various internal diameters to be introduced in order to vary the rate at which equalisation of pressure in the tube and reservoir took place. An experiment was conducted as follows. The tube was exhausted to a pressure below 2 cm., and connected to the reservoir by turning the three-way cock as rapidly as possible; an observer, looking through the

FIG. 1.



sealed end of the tube (shielded by a plate of glass), reported whether ignition had or had not taken place.

Shock Ignition.—Preliminary experiments, using 5 to 15 per cent. mixtures of ether in air and a tube 2 cm. in diameter, gave results varying with the diameter of lead used. It was also found that changing the length of the tube from 50 to 100 cm. affected the temperature at which ignition was obtained. These irregularities were presumably due to the differences in time taken to fill the tube with the gas-mixture. Accordingly, a tube 7.5 cm. in diameter was substituted for the one previously used, so that the effect of changing the diameter of the lead could be investigated more easily. With a lead of 1 mm. diameter, ignition took place

ETHER-ALCOHOL-AIR AND ACETONE-AIR MIXTURES, ETC. 1469

at temperatures near 200° , but, on using a lead of 5 mm. in diameter, it was found possible to obtain ignition at from 50° to 60° . These results were obviously too low, and observation showed that they were influenced by the position of the end of the tube relative to the furnace. Experiments were carried out to elucidate this phenomenon, and it was found possible to ignite ether-air mixtures at the ordinary temperature and to ignite other gaseous mixtures at temperatures well below those commonly considered as their ignition-temperatures. The apparatus used consisted of a glass tube 7.5 cm. in diameter, which was connected to a reservoir of 16 litres capacity by means of a glass lead 80 cm. long and of 1.9 cm. internal diameter. By using on the reservoir a cock of 1.5 cm. bore, it was possible to equalise the pressure in the two portions of the apparatus very suddenly. Under these conditions, it was found that when the tube and lead were exhausted and kept at the same temperature as the reservoir (16.5°), ether-air mixtures containing 5 to 15 per cent. of ether were ignited on opening the reservoir cock.

The ignition invariably took place within 15 cm. of that end of the tube remote from the reservoir. In most cases it resulted in a pale blue flame, which travelled quietly along the tube, but sometimes gave inflammation sufficiently violent to shatter the glass. When using 7.5 cm. tubing, ignition could be obtained easily with 60 and 90 cm. lengths, even when the pressure in the reservoir was less than half the atmospheric. Ignition occurred in a 150 cm. tube only when the pressure in the reservoir was greater than three-quarters of an atmosphere. When a 300 cm. tube was used, no ignition could be obtained at the ordinary temperature; a similar negative result was obtained with bottles 30 cm. long and 11.2 to 12.5 cm. in diameter, that is, of approximately the same capacity as the 90 cm. tube. A pad of soft leather in the closed end of a tube of optimum length seemed to prevent ignition at the ordinary temperature, and a plug of cotton wool prevented ignition in precisely the same way. Replacement of the 7.5 cm. tube by one 2 cm. in diameter brought about the same result. It appeared to be immaterial whether highly purified ether or the ordinary commercial variety was used for these experiments. Amongst the other gases tested were mixtures of hydrogen and the vapours of acetone and carbon disulphide with air. Dilute carbon disulphide-air mixtures ignited at the ordinary temperature, acetone-air mixtures below 250° , and hydrogen-air mixtures below 450° , but these experiments were not continued. The information at present available makes it appear highly probable that this ignition is due to the shock caused by the sudden

stoppage of the gas rushing into the exhausted tube. In this connexion, a statement made by Sir Charles Parsons in his inaugural address at the Bournemouth Meeting of the British Association (1919) is of interest. This was to the effect that during the work of a committee appointed by the Admiralty in 1916 to investigate the cause of abnormal propeller erosion, it was discovered that by allowing water to rush into an exhausted conical vessel, a pressure of more than 220 kilos. per sq. mm. was recorded at the apex of the cone. That ignition of a gas-mixture can be produced by a compression wave was demonstrated by Bradshaw (*Proc. Roy. Soc.*, 1907, [4], 79, 236) for mixtures of carbon disulphide in oxygen and for electrolytic gas.

Another factor, the actual rarefaction, must not be forgotten. Investigations by Mitscherlich (*Ber.*, 1893, 26, 399) on the temperature necessary to explode mixtures of hydrogen and oxygen seem to show that the explosion point is reduced very appreciably by lowering the pressure. Again, Labillardiere, Friedel and Ladenburg, Stock and Guttman, and others have shown that the temperature necessary for the ignition of mixtures of the hydrogen compounds of phosphorus, silicon, and antimony with oxygen is presumably lowered by reducing the pressure, and that explosion has been known to follow sudden rarefaction. In the course of the work described in this paper, the maximum reduction in sub-ignition-temperature of ether-air mixtures apparently obtained by reduction in pressure alone was only 7° , that is, from 187° to 180° , as shown in Fig. 4. This appears to leave a fair margin for other factors.

The importance of this "shock" ignition is obvious whether it be considered from the theoretical or practical point of view, and it may quite well account for hitherto obscure ignitions met with in the course of solvent-recovery and mine work. The phenomenon underlying shock-ignition must also invalidate a good deal of research work.

Attempt to Eliminate Shock-ignition.—One conceivable method of avoiding shock-ignition in the determination of sub-ignition-temperatures would appear to be that in which the gas is given no appreciable flow before being stopped. An attempt to realise these conditions was made by joining a small bulb on to a gas reservoir in such a way that the distance between the bulb and reservoir was as small as possible. A three-way tap was inserted between the reservoir and bulb to enable the bulb to be exhausted before an experiment. The bulb, which was made of glass, was kept at any desired temperature by being almost entirely immersed in a bath of mercury. When once a connexion had been made

between the bulb and gas reservoir, the tap was turned so as to close both bulb and reservoir. If ignition took place, a flash was easily observed where the bulb-stem emerged from the bath. The bore of the bulb-stem was varied in different determinations. The results obtained when using a 4.5 per cent. mixture of ether in air are given in table I. From them, it will be noticed that the effect of the size of lead is not completely eliminated by this method.

TABLE I.

Showing the Sub-ignition-temperatures of a 4.5 per cent. Ether-Air Mixture obtained by the Bulb Method, using Various Leads.

Diameter of bulb in cm.	Sub-ignition-temperature when lead was		
	Ordinary tube.	Capillary.	Fine capillary.
4.8	178.0°	181.0°	184.0°
4.1	179.0	184.0	185.0
3.5	180.5	185.5	188.0

An interesting point observed in these experiments was the fact that when using a 4.5 per cent. mixture near its apparent ignition-temperature, explosion invariably occurred. On the other hand, when using the bulbs specified above with an ordinary capillary lead and the same gas-mixture, on no occasion did an explosion take place when the temperature of the bath was greater than 197°. Above this temperature, a luminous flash was observed, and nothing more. A 6 per cent. mixture gave similar results, but a 10 per cent. mixture gave no explosion at any temperature tried. An 8 per cent. mixture behaved in precisely the same way as a 10 per cent. mixture, except that on one solitary occasion a violent explosion shattered the bulb. It is possible that a good approximation to the correct sub-ignition-temperature could be obtained by using a very fine capillary tube and a fairly large bulb, but the experiment would not be without danger.

Final Apparatus.—It was found that by making use of a fairly long tube and allowing the sealed end to project well out of the furnace, effects of shock-ignition were apparently eliminated. In this case, the point at which shock-ignition would have occurred in normal circumstances was well outside the heated zone, and on no one occasion was an ignition in the final apparatus observed to start outside the furnace. The lengths of tube used were as follows:

2 cm. tube.	100 cm.
4 cm. tube.	130 cm.
5.5 cm. tube.	130 cm.

The chief difficulty encountered was that of deciding when an ignition had occurred. This was generally easy in the case of

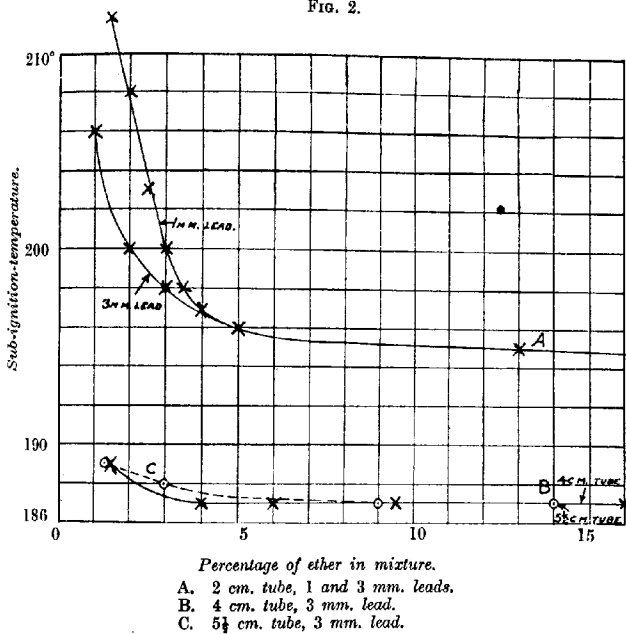
shock-ignition, as not only was the flame fairly easily seen, but the products of combustion had a characteristic and powerful odour. In the case of dilute mixtures of ether in air and ether-alcohol-air mixtures containing small quantities of ether, however, the matter was quite otherwise. It was found almost impossible to distinguish between an ignition and the glow given below the sub-ignition-temperature by combustion on the surface of the glass until travelling was taken as the criterion. This was, of course, due to the fact that the ignition at the lowest possible temperature of a mixture containing ether and air invariably commenced with what has been termed the cool flame. This flame often requires a completely darkened room in order to be visible, but whenever any appreciable quantity of combustible mixture is present, it is liable to develop more or less rapidly into ordinary combustion and, possibly, detonation. That the volume of mixture present is an important factor can be seen from the fact that on no occasion did ordinary combustion develop in the 2 cm. tube within 150° of the sub-ignition-temperature. On the other hand, when using mixtures containing from 5 to 10 per cent. of ether in either of the other tubes, ordinary combustion was liable to develop, and certainly did develop if the temperature was a few degrees above that necessary for inflammation. Test experiments carried out with and without the thermo-couple and thermometer in the tube showed that the presence of these instruments did not appear to affect the result obtained.

Fig. 2 gives the results obtained for the sub-ignition-temperatures of various ether-air mixtures. It will be noticed that in the case of the 2 cm. tube, the results for dilute mixtures differ slightly according to the lead used. This is presumably due to the fact that combustion takes place to a relatively greater extent in the case of the smaller lead, making it more difficult to see the flame at the same temperature. On the other hand, above a certain limit, the internal diameter of the lead does not appear to affect the results obtained with the other tubes. Surface action appears to be negligible in the case of ether-air mixtures of any appreciable concentration if the tube has a diameter of at least 4 cm. That the longer time taken to heat the larger bulk in a wide tube made little difference in the case of ether-air mixtures of concentration greater than about 4 per cent. was proved by adding 1.5 per cent. of the products of combustion of an ether-air mixture to a 5 per cent. mixture of ether in air. The sub-ignition-temperature was only raised 2° . It was found that no difference in sub-ignition-temperature could be detected when purified ether was replaced by the commercial article. It is interesting to note from the shape

of the curve in Fig. 2 that the ignition of ether-air mixtures by this method, depending as it does on the preliminary production of the cool flame, appears to be a molecular process requiring only a certain intensity of molecular movement for its production. The form of curve connecting minimum igniting current with composition of ether-air mixture appears to be quite different.

In Fig. 3 can be seen the sub-ignition-temperatures of certain ether-alcohol-air mixtures as determined in the 2 cm. and 4 cm.

FIG. 2.

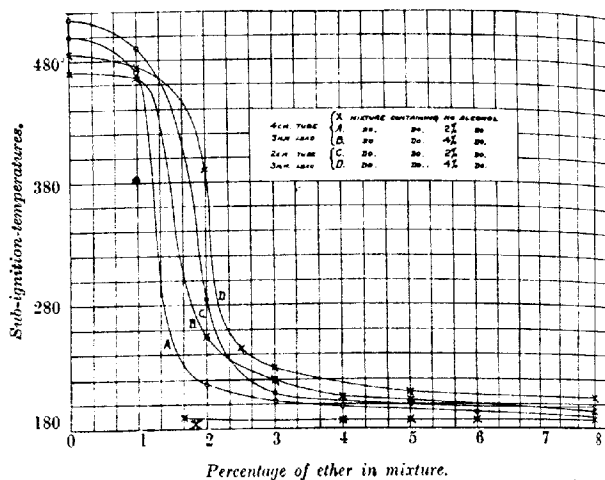


tubes. The number of points shown on each curve is not great, owing to the fact that the general form of the curves had been previously found when using smaller leads. Each point on the diagram is the mean of three determinations agreeing to within 2° in the case of temperatures below 220° and to within 5° in the case of temperatures above this point.

A consideration of the results given shows that the sub-ignition-temperature of an ether-alcohol-air mixture falls very rapidly when the amount of ether in the mixture is increased from 1 to 2

per cent. This drop is seen to take place with a smaller percentage of ether in the case of the 4 cm. tube, and in both tubes with a smaller percentage of ether in the case of the mixture containing the smaller amount of alcohol. The curves also indicate the manner in which the addition of alcohol to an ether-air mixture affects the sub-ignition-temperature. The elevation in sub-ignition-temperatures is roughly proportional to the amount of alcohol present provided the ether-content lies between 2 and 5 per

FIG. 3.



cent. For comparison, some results, obtained with 4 and 5.5 cm. tubes, are given in table II.

TABLE II.

Showing the Sub-ignition-temperatures of Various Ether-Alcohol-Air Mixtures containing 2 per cent. of Alcohol, as determined in 4 and 5.5 cm. Tubes.

Percentage of ether in mixture.	Sub-ignition-temperature for		
	5.5 cm. tube.		4 cm. tube.
	5 mm. lead.	3 mm. lead.	3 mm. lead.
1	495°	500°	470°
2	220	222	217
3	207	210	203
5	201	205	197

The sub-ignition-temperature determined with the 5.5 cm. tube is seen to be higher in every case than that obtained with the 4 cm. tube. This is probably due to the fact that, owing to the larger diameter of this tube, the time of heating is necessarily longer, and hence slow combustion occurs more readily.

With this tube, too, a slight but perceptible difference in sub-ignition-temperature is obtained when using 3 mm. and 5 mm. leads, as shown in table II.

It was seen that in the case of dilute mixtures of ether in air the size of lead used, if small, affected the temperature obtained. This effect was exceedingly marked in the case of ether-alcohol-air mixtures containing little ether. With small leads, it was found impossible to obtain consistent results. For instance, for a mixture of 2 per cent. of alcohol and 1.25 per cent. of ether in air, when using a 1 mm. lead with the 4 cm. tube, a flash would occasionally be obtained below 300°, but one could only be certain of an ignition well above 400°. It was found, however, that if the cock connecting the tube and reservoir was turned on slowly, no ignition was ever obtained below 400°. These differences vanished when leads of 3 mm. or more were used.

The sub-ignition-temperatures of various alcohol-air mixtures are given in table III.

TABLE III.

Showing the Sub-ignition-temperatures of Various Alcohol-Air Mixtures as determined in 2 cm., 4 cm., and 5.5 cm. Tubes.

Percentage of alcohol in mixture.	Sub-ignition-temperature for		
	2 cm. tube (3 mm. lead).	4 cm. tube (3 mm. lead).	5½ cm. tube (5 mm. lead).
2	515°	500°	520°
3	505	490	505
4	485	470	500
5	480	465	495

In the 4 cm. tube an explosion was often obtained with 4 and 5 per cent. alcohol-air mixtures at 485°. The evidence as to the slower heating of the gaseous mixture in the largest tube is confirmed by the figures given here, as the temperatures found in the case of the largest tube are higher than those for the smallest. It thus appears from the above figures that the nearest possible approach to the correct sub-ignition-temperature of an ether-alcohol-air mixture is obtained by means of a 4 cm. tube. It was found that almost identical results were obtained in the 2 cm. and 4 cm. tubes, whether 2 or 3 mm. leads were used, and that it was not important whether a 3 or 5 mm. lead was used for the

5.5 cm. tube. The sub-ignition-temperatures considered most likely to be correct are summarised in table IV.

TABLE IV.

Showing the Sub-ignition-temperatures of Various Ether-Alcohol-Air Mixtures.

Percentage composition of mixture by volume.			Sub-ignition-temperatures.
Ether.	Alcohol.	Air.	
3—15	0	97—85	187°
8	2	90	189
4	2	94	198
3	2	95	203
2	2	96	217
1	2	97	470
8	4	88	194
4	4	92	206
3	4	93	220
2	4	94	255
1	4	95	465
0	2	98	500
0	3	97	490
0	4	96	470
0	5	95	465

The sub-ignition-temperatures of some acetone-air mixtures as determined in tubes of various diameters were found to vary in a manner similar to those of alcohol-air mixtures. The results given below were obtained when using a tube 4 cm. in diameter with a 3 mm. lead.

TABLE V.

Showing the Sub-ignition-Temperatures obtained for some Acetone-Air Mixtures.

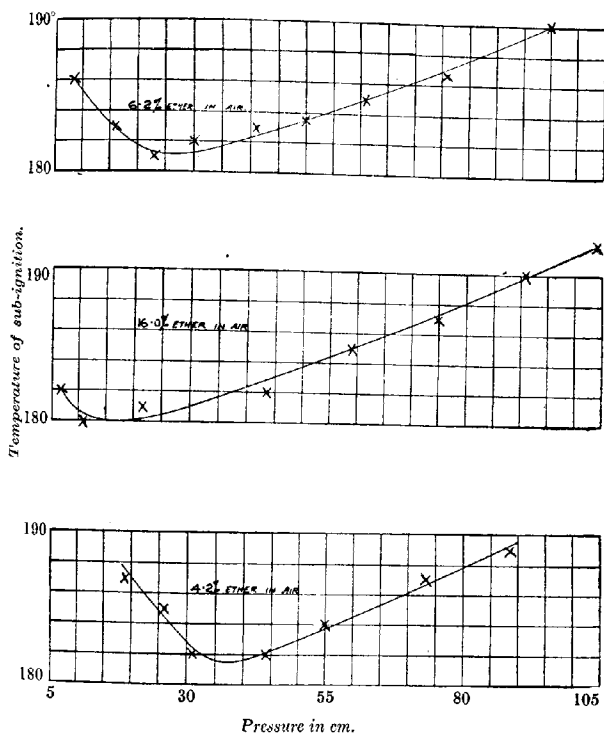
Percentage of acetone in acetone-air mixture.	Sub-ignition-temperature.
4	500°
8	500
Saturated at 15°	505

The ignition found for acetone was very faint at the sub-ignition-temperature, but grew in intensity very rapidly as the temperature of the tube increased.

Influence of Pressure.—During the course of preliminary work on the determination of sub-ignition-temperatures of ether-air mixtures, it was found that consistent results were not obtained for successive experiments when the mixture in the reservoir was not renewed after each determination. This was apparently due to change of pressure inside the reservoir. Several experiments

were therefore made in which the pressure in the reservoir was reduced by pumping out the gas-mixture before firing, and it was found that when the pressure in the reservoir after an experiment was plotted against the sub-ignition-temperature determined, the curves shown in Fig. 4 were obtained. Other mixtures tested in the same way gave precisely similar results, and it was finally found

FIG. 4.



that the easiest method of determining the accurate sub-ignition-temperature of any given mixture under 760 mm. pressure was by starting with a gas-mixture under about 900 mm. pressure and plotting a small portion of the pressure-sub-ignition-temperature curve. The results given in Fig. 2 were obtained in this way. It will be observed that the minimum sub-ignition-temperature

appears to be given at a lower pressure in the case of a mixture rich in ether than in the case of a dilute mixture. This is probably due to the fact that there is a minimum quantity of ether per unit volume necessary to give visible luminosity under any given conditions.

Influence of the Material of the Tube.—A consideration of the results obtained with various tubes shows that it was impossible to eliminate surface action entirely, probably owing to the fact that in the case of the larger tube the heating of a body of gas is necessarily slower. It thus became a matter of importance to discover whether the material of the tube had any influence on the result obtained. The simplest method of effecting this appeared to be by fitting a glass tube with a thin sleeve of the material under test. Accordingly, the 4 cm. tube was fitted with sleeves long enough to project beyond the furnace on either side, these sleeves being made of various metals that might conceivably be used in a manufacturing plant in the presence of gas-mixtures such as those considered. The results obtained are given in table VI.

TABLE VI.

Showing the Results obtained for the Sub-ignition-temperature of Ether-Air and Alcohol-Air Mixtures in a 4 cm. Tube provided with an Internal Metallic Sleeve.

Material of sleeve.	Sub-ignition-temperature.		
	4.3 per cent. of ether in air.	10.5 per cent. of ether in air.	5 per cent. of alcohol in air.
Glass	187°	187°	465°
Copper	175	175	420
Iron	178	178	400
Lead	180	180	—
Zinc	184	184	—
Galvanised iron	184	184	—

The figures given for copper and iron in the case of the alcohol-air mixture can only be regarded as rough approximations, owing to the rapidity with which these metals oxidised at the temperature necessary for ignition. When the metal was oxidised to any appreciable extent, different results were obtained. For instance, the sub-ignition temperature in the case of a copper sleeve oxidised in the course of ten experiments was 470°. In the case of both ether-air and alcohol-air mixtures, the ignition commenced as a cool flame, but was invariably more violent in the presence of metals, more particularly copper and iron, than with glass.

Influence of the Velocity of the Gas-mixture.—As the gases dealt with in solvent-recovery are generally in motion, it was

decided to investigate to some slight extent the effect of the velocity factor on the sub-ignition-temperatures obtained. Arrangements were therefore made by which the gas-mixture in a reservoir could be displaced by means of water, and the gas from this reservoir made to displace the contents of a second reservoir. The gas-mixture from this second reservoir was passed into a 4 cm. tube 120 cm. long, which was kept at any desired temperature by means of an electric furnace. The far end was partly closed by means of a thick glass plate. It was found that once a steady state had been attained, the velocity of the gas in the tube could be measured sufficiently accurately by estimating the rate at which water was introduced into the first reservoir. An observer looking through the plate glass could easily see if ignition occurred. The sub-ignition-temperature for zero velocity was taken to be the lowest temperature at which ignition occurred after the gas supply had been cut off. The results obtained for two ether-air mixtures are given below in table VII.

TABLE VII.

Showing the Effect of the Velocity of the Gas-mixture flowing through a 4 cm. Tube on the Sub-ignition-temperature observed.

4.5 per cent. of ether in air.		14 per cent. of ether in air.	
Velocity in cm. per second.	Sub-ignition- temperature.	Velocity in cm. per second.	Sub-ignition- temperature.
0	187°	0	186°
6.0	195	1.0	189
12.5	202	5.5	195
—	—	8.0	197
—	—	13.0	202

The experiments carried out were sufficient to indicate that for very small velocities, increase of velocity causes an elevation of the sub-ignition-temperature observed. The velocities dealt with on the manufacturing scale are, however, of a totally different order, ranging from 100 to 400 cm. per second in various pipes.

Influence of the Presence of Glyceryl Trinitrate, Ethyl Hydrogen Peroxide, and Diethyl Peroxide in the Ether Used.—Several attempts were made to find if the presence of glyceryl trinitrate in an ether-air mixture affected the sub-ignition-temperature. In no case was any such effect discernible. In the experiments for which the results are given in table VIII, the glyceryl trinitrate was introduced into the reservoir by passing the air used for making up the mixture through a calcium chloride tube in which glyceryl trinitrate was spread over glass wool, the tube and contents being

kept at 40° to 45°. Results obtained in a 2 cm. tube were similar to those given below, which were determined by using a 4 cm. tube.

TABLE VIII.

Showing the Effect of the Presence of Glyceryl Trinitrate, Ethyl Hydrogen Peroxide, and Diethyl Peroxide on the Sub-ignition-temperature of Ether-Air Mixtures.

Composition of Mixture.	Sub-ignition-temperature.
5.3 per cent. of ether in air	187°
5.3 per cent. of ether and 1.5 per cent. of diethyl peroxide in air	189
3.7 per cent. of diethyl peroxide in air	189
4.7 per cent. of ether and 0.5 per cent. of ethyl hydrogen peroxide in air	182
5.3 per cent. of ether in air saturated with glyceryl trinitrate at 20°	187

The presence of glyceryl trinitrate did not appear to affect the flame given by the mixture, but the presence of the peroxides caused a very fierce flame and generally an explosion.

It was considered inadvisable to try to determine the sub-ignition-temperature of ethyl hydrogen peroxide in air. The peroxides were found to be exceedingly dangerous to handle; even diethyl peroxide exploded violently on one occasion during distillation.

SECTION II.

The Limits of Propagation of Flame in Ether-Alcohol-Air and Acetone-Air Mixtures.

Many references are to be found in the literature to the limits of inflammability of mixtures of ether and alcohol with air, and some figures are also given for acetone-air mixtures. The limits determined by various workers are given below.

Ether-Air Mixture.—Limits of inflammability.

2.7 to 7.7 per cent. by volume (Brunswick, "Explosives," first edition, 1912, p. 73).

50 to 60 grams per cubic metre for lower limit (Marchis, *Mét. and Chem. Eng.*, 1916, **14**, 190).

2.9 to 7.5 per cent. by volume (Lewes, *J. Soc. Arts*, 1915, 761).

2.9 to 7.5 per cent. by volume (Schwartz, "Fire and Explosion Risks," first edition, p. 35).

0.058 to 0.195 gram per litre (Meunier, *Compt. rend.*, 1907, **144**, 1107).

Alcohol-Air Mixture.—Limits of inflammability.

4.0 to 13.7 per cent. by volume (Brunswig, *loc. cit.*).

4.0 to 13.6 per cent. by volume (Lewes, *loc. cit.*).

3.95 to 13.65 per cent. by volume (Bunte and Eitner, *J. Gasbeleucht*, 1901, **44**, 835).

3 to 8.4 per cent. by volume (Thornton, *Proc. Roy. Soc.*, 1914, [4], **90**, 280).

Acetone-Air Mixture.—Limits of inflammability.

5 to 12 per cent. by volume (Brunswig, *loc. cit.*).

2.15 to 9.7 per cent. by volume (Wheeler and Whitaker, *T.*, 1917, **111**, 267).

It will be seen that the results obtained vary considerably, owing to the different conditions under which the experiments were carried out and the various igniting sources used. This is to be expected, as the conditions governing the propagation of flame were not properly appreciated until recent years. The definition now adopted is that suggested by Coward and Brinsley (T., 1914, **105**, 1859), in which inflammability is regarded as a specific property of a mixture, independent of the size and shape of the vessel in which it may happen to be contained, and also of any particular type of igniting arrangement. They propose to define a gaseous mixture as inflammable *per se* at a stated temperature and pressure if, and only if, it will propagate flame indefinitely, the unburnt portion of the mixture being maintained at the original temperature and pressure. On this definition, inflammability is a property of the mixture itself, although a function of the temperature and pressure. Dilution-limits, however, rarely vary much throughout the usual range of variation of laboratory temperature and pressure. It will thus be seen that, in order to obtain satisfactory results in the estimation of dilution-limits, it is necessary to use a vessel (1) of such size that any cooling of the gas-flame by the walls can be neglected, and (2) of sufficient length to enable a sound judgment to be made as to whether a flame would propagate indefinitely or no.

For every gas-mixture examined, propagation-limits were determined for three directions—upward, horizontal, and downward.

Preliminary work seemed to indicate that in a glass tube 5 cm. in diameter, by using a sufficiently powerful initiator, it was possible to force a flame through a mixture below the limit of propagation to the end of the tube, unless it was at least 120 cm. long. All the tubes for limit work were therefore made at least 150 cm. in length.

The tubes consisted of:

(1) Glass tubes 2.5 cm. in diameter.

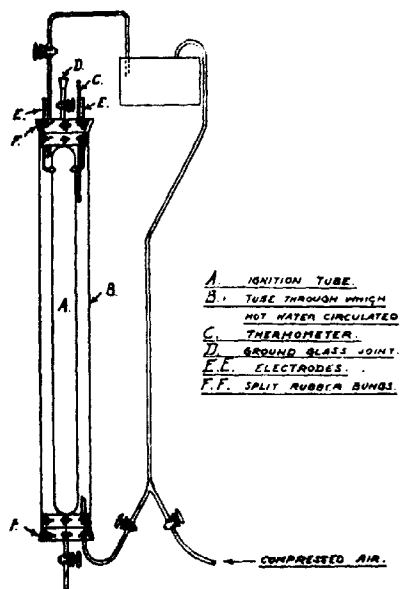
- (2) Glass tubes 5 cm. in diameter.
- (3) An iron * tube 5 cm. in diameter.
- (4) An iron tube 15 cm. in diameter and 300 cm. long.

The glass tubes and the 5 cm. iron tube were 150 cm. long. The glass tubes were closed at both ends by gas-tight stopcocks of 4 mm. bore, and a similar cock was fitted to one end of the iron tube, where a 5 cm. glass observation piece was cemented for observation purposes. The cocks, in the case of the 15 cm. iron tube, were of brass and of 6 mm. bore. In this tube, inflammation was observed through three equidistant windows of thick plate glass, which were cemented into holders on the tube. These windows gave much trouble, and it was found impossible to render them gas-tight by using cement alone. Accordingly, caps were soldered over each window in such a way that, by inserting a 3.7 cm. rubber stopper into the observation hole left in the cap, the whole apparatus could be made gas-tight. The stoppers were removed immediately before firing. This tube was filled by means of a filler similar to that shown in Fig. 1, the end of the filler being made to project well through a tightly fitting piece of rubber tubing drawn over one of the cocks. The filling was carried out precisely as described previously, a correction being always applied for the vapour of the solvent present in the air above the liquid in the filler. In the case of all the smaller tubes, the fillers were provided with ground-glass joints fitting pieces sealed on to the tubes concerned. All the air passed in to make up any mixture containing alcohol or acetone was carefully dried by passage through a calcium chloride tube. The calibration of the tubes was carried out by weighing the quantity of water necessary to fill them. Ignition was effected by passing a spark from an induction coil between two electrodes of stout platinum wire separated by an air gap of 1 cm., the current being obtained from six 2-volt accumulators. In the glass tubes originally used, the platinum was sealed through the glass, but as good sealing glass became scarce, this was found to be impracticable, and the electrodes used for all the tubes consisted of platinum in glass mounted in rubber stoppers. The original method of mixing the gases was by allowing the tube to remain for several hours, but this became inadvisable when rubber was brought into contact with the solvent-laden air. A little mercury enabled efficient mixing to be carried out by shaking the tube, but it was found that this affected the results obtained, and, finally, small glass beads were used. Com-

* This, and the other iron tubes used in the investigation, consisted of tenné plate, that is, sheet-iron coated with an alloy of lead and tin.

parative tests showed that, when using an adequate number of beads, shaking a 5 cm. tube for twenty minutes gave satisfactory mixing. It was also shown that, under these conditions, the same results were obtained whether the electrodes were held by small rubber stoppers or were sealed through the glass. Throughout the course of the work, the only tube that caused trouble was the 5 cm. iron tube. The various cements used for fastening the glass observation cap to the main body of the tube seemed to hold solvent, and the results obtained for this tube cannot be considered

FIG. 5.



as trustworthy as those obtained with the others. The mixing of the contents of the 15 cm. iron tube was done very efficiently by rolling a 12.5 cm. perforated hollow copper ball from end to end.

The apparatus used for determining the upper limit of propagation for alcohol-air and certain ether-alcohol-air mixtures consisted of a 5 cm. glass tube jacketed by enclosure in a wider glass tube, so that hot water could be continuously circulated round it. The arrangement used is shown in Fig. 5.

Two sets of this apparatus were fitted up, one as shown in the

sketch, arranged for experiments on downward propagation, with the electrodes at the same end of the tube as the ground-glass joint for filling the tube, and the other arranged for upward propagation, in which the electrodes were at the end away from the ground-glass joint. For horizontal propagation, either of the above tubes was used and placed horizontally before firing. Some difficulty was encountered in sparking the mixtures contained in this apparatus, but by enclosing the leads in glass tubes, this was finally overcome. Naturally, mixing in these tubes could only be accomplished by allowing the tube to remain for some time.

The procedure in the case of any mixture can be seen by a consideration of the results given below.

Experiment 21.—Glass tube, 5 cm. in diameter.

Solvent mixture used, 75 per cent. of ether and 25 per cent. of alcohol (by weight).

Lower limit, downward propagation. Temperature, 19°.

Percentage of solvent-vapour in gas-air mixture (by volume).

2.70	Complete ignition.
2.40	Flame just started.
2.60	Complete ignition.
2.50	Partial ignition.
2.55	Flame went nearly to the end.
2.57	Flame went very slowly to the end.

Limit—2.57 per cent.

In the case of a lower limit, an accuracy of 0.02 per cent. was aimed at; in the case of an upper limit, 0.05 per cent. was taken. In every instance, just before firing, the cock furthest removed from the electrodes was opened to allow a free passage for the gases. When the limit of propagation was being determined for a mixture of ether and alcohol, a liquid containing the requisite proportions of these two solvents was made up and used. A test experiment showed that this gave the same result as was obtained when the two solvents were weighed into the tube separately.

Ether-Alcohol-Air Mixtures.—The results obtained for ether-alcohol-air mixtures in glass tubes are shown in table IX.

The experimental results obtained with the 2.5 cm. tubes are not so trustworthy as those determined in larger tubes, as can be seen from the results themselves. For example, the result obtained for the lower limit of an ether-air mixture is least for downward propagation, and other anomalies could be pointed out in the same way. These irregular results were probably due to the fact that it was only for downward propagation that the flame travelled more or less steadily. For upward propagation, it was sometimes

TABLE IX.
Showing the Limits obtained for the Propagation of Flame in Ether-Alcohol-Air Mixtures as determined in Glass Tubes.

The limit figures given show the percentage volume occupied by the total ether-alcohol vapour.

Percentage composition of mixture (by weight).		Diameter of tube in cm.	Direction of propagation.					
			Upwards.		Horizontally.		Downwards.	
Ether.	Alcohol.		Upper limit. Per cent.	Lower limit. Per cent.	Upper limit. Per cent.	Lower limit. Per cent.	Upper limit. Per cent.	Lower limit. Per cent.
100	0	2.5	18.50	2.35	6.15	2.38	6.30	2.34
75	25	"	6.95	3.15	7.35	3.36	7.35	2.99
50	50	"	—	3.52	—	3.39	—	3.58
25	75	"	—	4.35	—	4.45	—	4.40
0	100	"	—	5.02	—	5.18	—	5.21
100	0	5	15.75	1.93	8.00	2.05	6.15	2.15
75	25	"	11.70*	2.40	10.95*	2.49	8.35*	2.57
50	50	"	10.70*	2.89	10.35*	2.99	9.25*	3.05
25	75	"	12.00*	3.53	11.50*	3.61	10.35*	3.71
0	100	"	18.95*	4.24	13.80*	4.32	11.50*	4.44

* The figures marked thus were determined in the jacketed tube at 60°, and are, for this reason, not strictly comparable with the others, which were determined at air-temperature (20° ± 2°).

obviously jerked out. Wheeler's work has shown that only a very slight change in the limits takes place when the diameter of the glass tube is increased beyond 5 cm., so that this was the largest size of glass tube used. His work, however, was chiefly carried out with permanent gases.

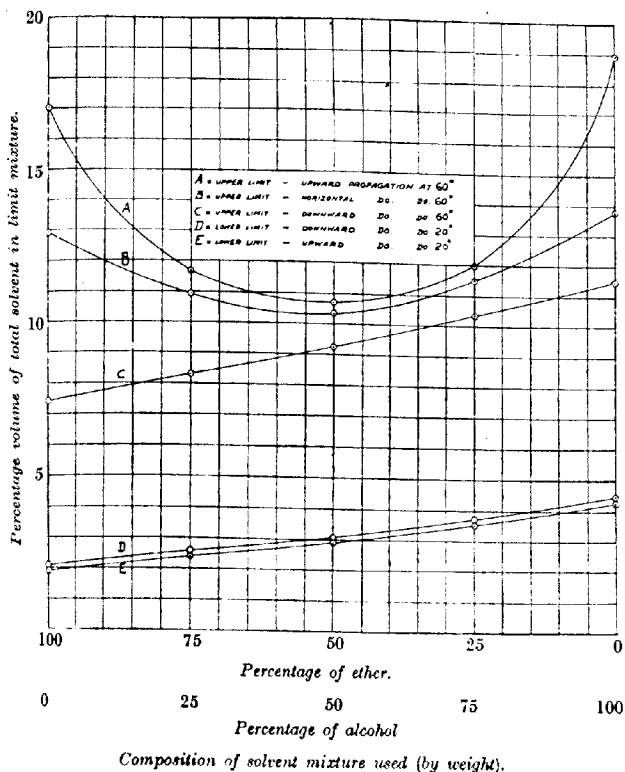
The most noticeable fact brought out in table IX appears to be the great difference between the results obtained for the upper limit for upward propagation and those obtained for propagation in other directions. These differences, which are normally due to convection currents set up by the flame, are not so great for permanent gases. The difference between the upper limits for horizontal and for upward propagation is most marked, and it almost appears as if a different type of propagation were brought into being. It is quite conceivable that the heated gases, rising in the tube, are responsible for the initiation of a cool flame. The difference is not so great in the case of alcohol as it is for ether.

The results for ether-alcohol-air mixtures in a 5 cm. glass tube are shown in Fig. 6. The results given for the upper limits were all determined at 60°. The graphed results for the lower limits and the upper limit for downward propagation form good approximations to straight lines, but this is not the case for the other two curves. At first sight, it seems very strange that, for the upper limit for upward propagation, the results for a mixture containing equal weights of ether and alcohol should be more than 6 per cent. less than the corresponding figure for either ether or alcohol. A possible explanation appears to be afforded by an examination of the sub-ignition-temperature curves given in Fig. 3. From these, it will be seen that the addition of alcohol to an ether mixture raises the sub-ignition-temperature so that the slope of the two upper curves near the 100 per cent. ether point is in the direction to be expected. Similarly, the slope near the 100 per cent. alcohol point can be explained when it is remembered that it takes an appreciable quantity of ether to cause any decided lowering of the sub-ignition-temperature of an ether-alcohol-air mixture. That there is no apparent irregularity corresponding with that seen when the percentage of ether is between 1 and 2 per cent. on the sub-ignition-temperature curves may be due to the fact that so few points have been determined on the limit curve; but it is far more likely to be due to the fact that the sub-ignition-temperature obtained for an ether-alcohol-air mixture containing, say, 2 to 2.5 per cent. of ether, is due solely to the ignition of the ether present, and that the alcohol takes little part in the reaction. These remarks do not apply to curve C, Fig. 6,

as in that case the flame obtained is undoubtedly that of ordinary combustion.

The limits of inflammability of a mixture of two or more gases with air are connected with the limits of the components of the mixture by Le Chatelier's rule, which states that if $n, n', n'' \dots$

FIG. 6.



are the percentages of various combustible gases in a limit mixture which will just propagate flame, and $N, N', N'' \dots$ the limiting percentages of the separate gases that can propagate flame, then

$$\frac{n}{N} + \frac{n'}{N'} + \frac{n''}{N''} + \dots = 1.$$

In table X are given the values for Le Chatelier's constant,

calculated from the results found for various ether-alcohol-air mixtures in 5 cm. glass tubes.

TABLE X.

Showing the Value obtained for Le Chatelier's Constant for Various Ether-Alcohol-Air Mixtures in 5 cm. Glass Tubes at $20 \pm 2^\circ$.

Limit.	Direction of propagation.	Value of constant in mixture of following percentage composition by weight.			Maximum percentage variation from unity.
		25 ether. 75 alcohol.	50 ether. 50 alcohol.	75 ether. 25 alcohol.	
Upper	Downwards	0.984	0.971	0.983	3
	Horizontal ...	0.833	0.774	0.830	33
	Upwards ...	0.646	0.589	0.663	41
Lower	Downwards	0.989	0.967	0.980	3
	Horizontal ...	0.995	0.985	0.992	1
	Upwards ...	1.004	0.993	1.007	1

The figures used for the upper limits in this table were all found at 60° , those for the lower being determined, as usual, within 2° of 20° . It will be seen that in all cases for the lower limit and for downward propagation in the case of the upper limit, Le Chatelier's rule holds for mixtures of ether and alcohol with air, and consequently the limits for a mixture containing any proportion of ether and alcohol can be calculated with an error of not more than 3 per cent. For horizontal and upward propagation, however, the rule breaks down entirely. As would be expected, the greatest deviation from the rule always occurs for a 50 per cent. mixture.

In table XI are given the results obtained when the same mixtures were ignited in 5 cm. and 15 cm. iron tubes. The upper limits for ether-air mixtures are given in table XII.

TABLE XI.

Showing the Results obtained in Iron Tubes of 5 and 15 cm. Diameter for the Lower Limits for the Propagation of Flame in Certain Ether-Alcohol-Air Mixtures at $20 \pm 3^\circ$.

Percentage composition of solvent mixture by weight.		Diameter of tube in cm.	Lower limits for propagation of flame.		
Ether.	Alcohol.		Upwards.	Horizontal.	Downwards.
100	0	5	2.24	2.29	2.34
100	0	15	1.73	1.80	1.93
75	25	15	2.24	2.30	2.46
50	50	15	2.81	2.89	3.02
25	75	15	3.48	3.53	3.69
0	100	15	4.16	4.23	4.37

TABLE XII.

Showing the Upper Limits for Propagation obtained for Ether-Air Mixtures in 5 and 15 cm. Iron Tubes.

Diameter of tube.	Value of limit and direction of propagation.		
	Upwards.	Horizontal.	Downwards.
5	15.45	7.95	6.70
15	23.30	22.30	6.50

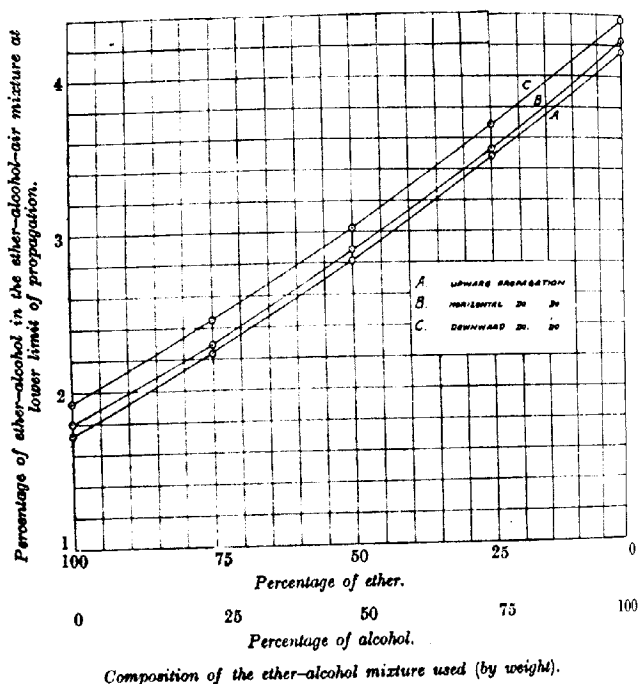
A comparison of these results with those given in table IX shows that for all three directions of propagation, the lower limit, as found for 5 cm. tubes, is greater when the tube is made of iron, as would be expected from the greater conductivity of this material. The reverse relation holds in the case of the upper limit obtained for ether-air for upward and horizontal propagation, but in the case of the downward propagation, the figure obtained for the iron is greater than that obtained for a glass tube of a similar size, or even for the 15 cm. iron tube. As this result appeared peculiar, a fresh determination of this limit was made, but the composition of the limiting mixture was found to be the same as that found in the first experiment. A comparison of the limits obtained in the 15 cm. iron tube with those previously determined (see tables IX, XI, and XII) is instructive. It will be seen that, in every case, the lower limit of a mixture is least in the case of the 15 cm. tube. The difference is very appreciable where a mixture contains a fair amount of ether, but is not so great where alcohol is present in excess. The upper limit, again, is always found to be greatest in the case of the 15 cm. tube, if we except the anomalous result obtained for downward propagation determined in the 5 cm. iron tube. These results may be due to a decrease in the cooling effect of the walls, or may possibly be due to turbulent motion in the gas caused by convection currents, as found by Wheeler and Mason (T., 1917, 111, 1044) in the case of velocity of flame. An item in favour of the latter supposition is provided by the exceedingly high figure obtained for the upper limit for horizontal propagation in the 15 cm. tube. On the other hand, the flame observed in the case of upward and horizontal propagation in the 15 cm. tube resembled very closely the cool flame of ether, and the characteristic odour following such a flame was observed. The lower-limit results for iron tubes are shown graphically in Fig. 7. The figures in table XIII show that Le Chatelier's rule holds moderately well for the lower-limit results obtained in the 15 cm. iron tube.

TABLE XIII.

Showing the Value Found for Le Chatelier's Constant from the Figures obtained for the Lower Limit for Propagation, using Ether-Alcohol-Air Mixtures in the 15 cm. Iron Tube.

Direction of propagation.	Values of constant given by mixture of percentage composition by weight shown.			Percentage maximum variation from unity.
	25 ether. 75 alcohol.	50 ether. 50 alcohol.	75 ether. 25 alcohol.	
Downwards	1.028	1.025	1.026	3
Horizontal	1.028	1.036	1.022	4
Upwards	1.039	1.038	1.031	4

FIG. 7.



Acetone-Ether-Air Mixtures.—Owing to the differences in results obtained for 5 cm. glass and 15 cm. iron tubes, particularly for ether-air mixtures, it was decided to determine the propaga-

tion of flame limits of certain ether-acetone-air mixtures in glass and iron tubes, as it was considered likely that results differing from those published by Wheeler and Whitaker (*loc. cit.*) for acetone-air mixtures would be obtained. The results of our experiments are shown in table XIV, those of Wheeler and Whitaker being given in table XV.

TABLE XIV.

Showing the Propagation of Flame Limits obtained for Acetone-Ether-Air Mixtures, using Various Iron and Glass Tubes at $20 \pm 2^\circ$.

Percentage composition of mixture by weight.		Material and diameter of tube.	Percentage of solvent in limit mixture and direction of propagation.					
Ether.	Acetone.		Upwards.		Horizontal.		Downwards.	
			Upper limit.	Lower limit.	Upper limit.	Lower limit.	Upper limit.	Lower limit.
0	100	Iron 5 cm.	—	3.80	—	3.90	—	4.00
0	100	Iron 15 cm.	12.40	2.88	12.40	2.89	10.90	3.11
0	100	Glass 5 cm.	12.20	2.89	9.15	3.04	8.35	3.15
25	75	„	11.20	—	8.55	—	7.75	—
50	50	„	11.70	2.34	8.25	2.39	7.25	2.49
75	25	„	13.20	—	8.15	—	6.65	—
100	0	„	15.75	1.93	8.00	2.05	6.15	2.15

TABLE XV.

Showing the Propagation of Flame Limits as determined by Wheeler and Whitaker for Acetone-Air Mixtures in Glass Tubes of Various Diameters.

Diameter of tube in cm.	Percentage of acetone in limit mixture and direction of propagation.					
	Upwards.		Horizontal.		Downwards.	
	Upper limit.	Lower limit.	Upper limit.	Lower limit.	Upper limit.	Lower limit.
2.5	7.5	2.30	6.7	2.40	6.5	2.75
5.0	9.5	2.20	9.3	2.25	8.3	2.40
10.0	9.7	2.15	9.5	2.20	8.5	2.35

It will be seen that our results differ considerably from those previously published. In most cases, they are considerably higher.

The explanation is almost certainly to be found in the fact that in our method the solvent was weighed directly into the tube, whilst in the other the acetone present in any mixture was estimated by analysis. That our method is the more accurate, as well as the easier, is obvious, but such a large discrepancy can only be explained by some abnormality in the behaviour of acetone during storage if the methods of analysis employed were not faulty. That such abnormal behaviour does take place when acetone vapour is stored over mercury is rendered extremely probable when the facts underlying the molecular association of acetone suggested in the paper by Wheeler and Whitaker are considered.

In this connexion, too, a quotation from the above paper might prove instructive. When discussing the analysis of the mixtures used, the following statement is made: "A supply of air was saturated with acetone vapour at 15° and 760 mm., when it contained 13.5 per cent. (by volume) of acetone, and used as a stock mixture from which the experimental mixtures could be prepared by the addition of air. . . . Consistent results were obtained by either of the absorption methods of analysis. Thus, a mixture, *known to contain about 6.5 per cent. of acetone*, gave on analysis:

"(1) Sodium hydrogen sulphite method . . . 6.50, 6.45, 6.54, 6.55.

"(2) Distilled water . . . 6.40, 6.56, 6.54, 6.50, 6.51, 6.51.

"Absorption by distilled water seemed, therefore, to afford a sufficiently accurate method of analysis."

The mixture "*known to contain about 6.5 per cent. of acetone*" was apparently made up by diluting the requisite quantity of the stock solution with a calculated volume of air. The accuracy of the method of analysis appears to be assumed from the fact that results approximating closely to the calculated figure were obtained. An examination of published figures for the vapour pressure of acetone at 15°, however, shows that a stock solution of air saturated with acetone vapour at this temperature at 760 mm. pressure would contain more than 19 per cent. of acetone (by volume), the vapour pressure of acetone at 15° being given by Sameshima (*J. Amer. Chem. Soc.*, 1918, **40**, 1482) as 147 mm. Extrapolation from Regnault's results gives a very similar figure—about 150 mm. Raising Wheeler and Whitaker's results in the ratio of 19:13.5 would often bring them much nearer to those obtained by us.

The results obtained for lower limits in the 15 cm. iron tube are strikingly similar to those obtained in a 5 cm. glass tube (see table XIV), and for upward propagation the upper limits are also very near. There are, however, very marked differences in the other figures given for the upper limits. It is worthy of note that

the upper limits for upward and horizontal propagation are here identical in the case of the 15 cm. tube. The results obtained when using the 5 cm. iron tube show clearly what a large effect the conductivity of the material of the tube has in this case. The results obtained in 5 cm. glass tubes for the propagation of flame limits of ether-acetone-air mixtures are shown graphically in

FIG. 8.

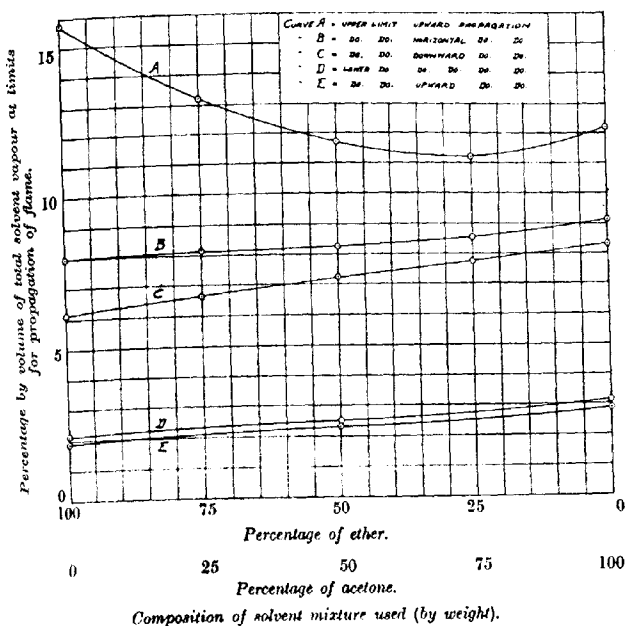


Fig. 8. It will be noticed that the upper-limit curves present the peculiarities commented on in the case of ether-alcohol-air mixtures, although to a less extent.

The figures given in table XVI show that Le Chatelier's rule holds moderately well for ether-acetone-air mixtures, except in the case of the upper limit for upward propagation.

TABLE XVI.

Showing Values obtained for Le Chatelier's Constant for the Limits for Propagation, using Ether-Acetone-Air Mixtures in the 5 cm. Glass Tube at $20 \pm 2^\circ$.

Limit.	Direction of propagation.	Value of constant given by mixture of percentage composition by weight shown.			Percentage [maximum variation from unity.
		25 ether. 75 acetone.	50 ether. 50 acetone.	75 ether. 25 acetone.	
Upper	Downwards	0.997	1.005	0.997	1
Upper	Horizontal	0.962	0.959	0.981	4
Upper	Upwards	0.875	0.866	0.910	13
Lower	Downwards	—	0.952	—	5
Lower	Horizontal	—	0.953	—	5
Lower	Upwards	—	0.987	—	1

Influence of Temperature.—The influence of temperature on the limits of inflammability of gaseous mixtures has been studied by Bunte and Roszkowski (*J. Gasbeleucht.*, 1890, **33**, 491, 524, 535, 553), Taffanel (*Compt. rend.*, 1913, **157**, 595), Burrell and Robertson (*United States Bureau of Mines, Technical Paper No. 121*, 1916), and Mason and Wheeler (*T.*, 1918, **113**, 45). The experimental work of Bunte and Roszkowski appears to have been defective, but the other workers found that the inferior limit of inflammability of methane-air mixtures was lowered by increasing the temperature of the gas-mixture before ignition. Mason and Wheeler also showed that the upper limit of inflammability of methane-air mixtures became much greater under these conditions, so that increasing the original temperature of the gas widens the limits of inflammability of methane-air mixtures. This would be expected from the fact that the self-propagation of a flame through a combustible mixture is only possible when the heat due to the reaction between the combining gases is sufficient to make up for losses due to radiation, conduction, and convection, whether the heat lost is dissipated or utilised in raising adjacent layers of the gas to the inflammation temperature. The heat of reaction necessary and the heat dissipated must obviously be less in the case where the original temperature of the gaseous mixture is higher. A few figures are given below to show to what extent the limits of inflammability are affected by temperature.

TABLE XVII.

Showing some Results obtained by Mason and Wheeler for the Downward Propagation of Flame in Mixtures of Methane and Air.

Initial temperature.	Lower limit.	Upper limit.
20°	6.00	13.40
100	5.45	13.50
200	5.05	13.85
300	4.40	14.25
500	3.65	15.35
700	3.25	18.75

In the circumstances, it was decided that it would be unnecessary to do more than find the change in the upper limit of ether-air mixtures with temperature. These experiments were carried out in the jacketed tube utilised for the upper limits of alcohol and ether-alcohol-air mixtures. The results obtained are shown in table XVIII. It will be seen that a decided rise in the upper limit for propagation takes place when the initial temperature of the mixture is raised through 40°.

TABLE XVIII.

Showing how the Upper Limit for the Propagation of Flame Varies with the Initial Temperature of the Ether-Air Mixture Used.

Direction of propagation.	Limit at 20°.	Limit at 60°.
Upwards	15.75	17.05
Horizontal ...	8.00	13.00
Downwards ...	6.15	7.45

Influence of Pressure.—The influence of pressure on the limits of inflammability of gases over any large range is by no means easy to predict, although it is well known that the lower limit of inflammability of many gas-air mixtures increases at diminished pressures. Terres and Plentz (*J. Gasbeleucht.*, 1914, 57, 990, 1001, 1016, 1025), Burrell and Robertson (*loc. cit.*), and Mason and Wheeler (*loc. cit.*) have investigated the effect of pressure on the limits of inflammability of mixtures of methane with air. The general conclusions to be drawn from their work appear to be that, below atmospheric pressures, decreasing the pressure narrows the limits of inflammability, but that above atmospheric pressure, increasing the pressure raises both the limits of inflammability.

The work done by us was confined to pressures at or below atmospheric pressure, and the results are shown in table XIX and XX.

TABLE XIX.

Showing the Influence of Pressure on the Limits for Horizontal Propagation of Flame in Ether-Air Mixtures.

Pressure in mm.	Percentage of ether in mixture.	
	At lower limit.	At upper limit.
770	1.87	—
751	—	12.90
600	—	10.50
520	—	9.20
460	1.88	—
450	—	8.20
420	—	7.90
400	—	7.80
300	1.92	7.30
200	2.08	6.80
100	2.33	6.10
50	2.99	5.00

TABLE XX.

Showing the Influence of Pressure on the Limits for Downward Propagation of Flame in Ether-Air Mixtures.

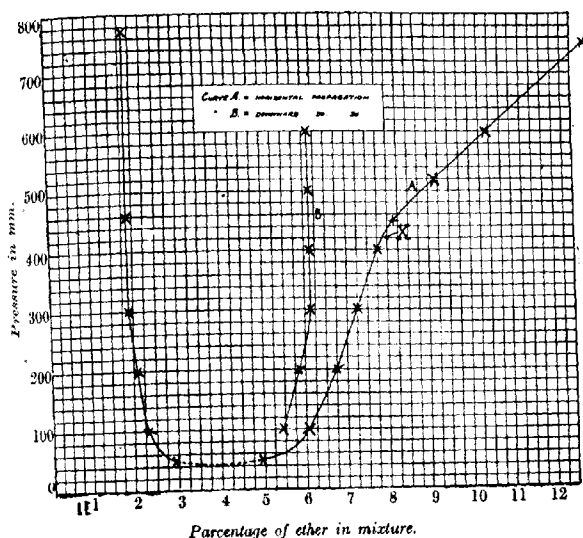
Pressure in mm.	Percentage of ether in mixture at lower limit.
600	6.20
500	6.20
400	6.20
300	6.20
200	5.90
100	5.50
50	No ignition.

It will be noticed that the results obtained near atmospheric pressure in the case of these experiments differ appreciably from those found by the ordinary method as given in table IX. This is due to the fact that all the experiments given in tables XIX and XX were carried out with both cocks closed. The type of ignition obtained was also very different; for instance, the ignitions obtained when determining the upper limit for horizontal propagation under 600 and 751 mm. pressure were characteristic, slow, cool flames which could not be seen except in a totally darkened room. It was found that any attempt to determine the limits for propagation of ether-air mixtures for pressures greater than atmospheric in the glass tubes available merely shattered the tube. The curves given by plotting pressure against the percentage of ether in the limiting mixture are given in Fig. 9. That for horizontal propagation is interesting. It was at pressures above that at the peculiar bend marked \times that the cool flame became notice-

able. Below this pressure the flame was of a green colour and traversed the tube very rapidly in a manner similar to that noticed for the lower limit at corresponding pressures.

Influence of Velocity.—Under present-day conditions of solvent-recovery, a good portion of the solvent-air mixture is often in rapid motion. It therefore became a question of determining, so far as was possible in the laboratory, the effect of velocity on the limits of propagation of solvent-air mixtures. Owing to the fact that no

FIG. 9.



real approximation to manufacturing conditions could be attained, the work done was confined to ether-air mixtures.

It has long been known that a moving mixture of combustible gas and air, too weak to propagate flame, can carry a cap of flame to a great distance from an igniting source. Wheeler has also proved that a mixture below the lower limit of propagation, when in a quiescent state, can often inflame when agitated. The speed of propagation of flame is also notably dependent on the degree of mechanical agitation of a mixture, and various experiments on the effect of agitation on gas-mixtures and on the rate of development of pressure when gas-mixtures are ignited are given by Clerk and

Hopkinson (*Rep. Brit. Assoc.*, 1912, 200), Clerk ("Ganet Lecture," Junior Institution of Engineers, 1913), and Wheeler (this vol., p. 81). So far as we know, however, no figures have as yet been given for the effect of the velocity of a gas-mixture on the limits of its propagation of flame.

The methods used for moving the mixture and determining its velocity were those described under sub-ignition-temperature. Great care had to be taken in determining the upper limit for propagation against the gas-current, as the flame passed with great velocity down the 10 mm. bent glass tube joining the limit tube to the reservoir. This gave very little time for preventing the flame from getting into the reservoir. The results obtained are given in table XXI.

TABLE XXI.

Showing the Effect of the Linear Velocity of an Ether-Air Mixture on its Downward Propagation of Flame Limits, as determined in a 5 cm. Glass Tube at $20 \pm 2^\circ$.

Flame moving in the direction of gas current.		
Velocity in cm. per sec.	Percentage of ether in mixture at lower limit.	Percentage of ether in mixture at upper limit.
0	2.13	6.15
1	1.97	6.40
3.5	1.95	6.50
9	1.95	6.65
Flame moving against the gas current.		
0	2.13	6.15
1	—	6.25
3.5	—	6.25
9	—	6.25

It was found to be impossible to find the lower limit of propagation when the flame was moving against the stream, as it merely became a question of the velocity of the stream as compared with that of the flame in the mixture used. It will be seen from the upper portion of the table that the velocity of the gas-current affects very appreciably the percentage mixture which will propagate flame. That a portion of this change is due to turbulence caused in the gas, however, appears to be very likely, for, in the cases tried, when the flame moves against the gas-current with any real velocity, the upper limit is always the same.

The figures given for zero velocity in table XXI are those found with one cock closed in the ordinary manner. As conditions are slightly different when both cocks are open, it was decided to try such an experiment. The upper limit found under these conditions

was 6.30 per cent., but the convection due to the flame probably caused this figure to be a little high, on account of the air drawn into the tube during the passage of the flame. It almost appears as if, when a flame is travelling against a gas-stream, the turbulence due to the velocity of the stream practically balances the effect of that velocity in hindering the propagation of flame.

Influence of the Presence of Glyceryl Trinitrate, Diethyl Peroxide, and Ethyl Hydrogen Peroxide.

In the experiments to determine the effect of glyceryl trinitrate on the limits of propagation for ether-air mixtures, the mixture used was charged with glyceryl trinitrate, as described under the experiments on the determination of sub-ignition-temperatures. The results obtained when using ether-air mixtures containing diethyl peroxide and ethyl hydrogen peroxide are given in table XXII.

TABLE XXII.

Showing the Effects on the Limits of Propagation of Flame of adding Amounts of Glyceryl Trinitrate, Diethyl Peroxide, and Ethyl Hydrogen Peroxide to Certain Ether-Air Mixtures.

Direction of propagation.	Limit.	Mixture used (with air).	Percentage of ether in limit mixture.
Upwards	Lower	Ether.	1.93
Downwards ...	"	"	2.15
"	Upper	"	6.15
Upwards	Lower	Ether saturated with glyceryl trinitrate at 20°.	1.95
Downwards ...	Upper	"	6.15
"	Lower	Diethyl peroxide.	2.34
"	"	Ether containing 25 per cent. of diethyl peroxide by weight.	2.18
"	Upper	"	10.1
"	Lower	Ether containing 10 per cent. of 80 per cent. ethyl hydrogen peroxide by weight.	2.17
"	Upper	"	6.5

The peroxides of ether are calculated as ether in making up the percentage volume occupied by the solvent in the limiting mixture. It will be seen that glyceryl trinitrate appears to have no effect on either limit, and that the peroxides have little effect on the lower limit, but that they raise the upper limit very appreciably.

The glyceryl trinitrate did not appear to affect the flames given, but the flames, when peroxides were present, were invariably fiercer than when ether alone was used, except, perhaps, at the extreme limit.

SECTION III.

Investigation of Various Means of Ignition.

A series of experiments was carried out in which sparks obtained by various means were used for attempting to ignite ether-alcohol-air mixtures. It was found that steel to steel, emery to steel, and pyrites to steel sparks appeared to be unable to cause the inflammation of any of the many mixtures tested. Ferro-cerium to steel sparks, however, ignited most mixtures very readily. The igniting powers of a small gas flame and a moderately powerful electric spark appeared to be of the same order, and both almost invariably gave rise to ordinary combustion, the limits of propagation of flame being naturally identical in the two cases. In the case of ether-alcohol-air mixtures, quick heating of a mixture, up to, but not far above, its sub-ignition-temperature, seemed to give rise to a cool flame which had limits for propagation varying from those of ordinary inflammation.

The Cool Flame.—The difference in propagation-limits for the two methods of combustion was particularly noticeable in the case of concentrated ether-air mixtures, as the flame travelled easily through a 20 per cent. mixture in a horizontal tube 4 cm. in diameter, although the upper limit for the propagation of ordinary combustion in a 5 cm. tube would be 8 per cent. No determinations of the limits for propagation of a cool flame were made, but experiments carried out for other purposes indicate that it is unlikely that such a flame could propagate downward through a mixture containing much more than 6 per cent. of ether. This flame was occasionally observed when electrical ignition was utilised, more particularly with high concentrations of ether or low pressures. It appeared, as stated by Perkin, to require very little oxygen, and the products of combustion were characteristic. It was found that the addition of less than 1 per cent. of oxygen to a mixture of 9 per cent. of ether in nitrogen was sufficient to give luminous combination below 220° . The increase of temperature caused by this flame in a mixture containing less than 3.5 per cent. of ether and heated to its sub-ignition-temperature was insufficient to be indicated by the fine thermo-couple registering the temperature of the gas in the ignition tube. The increase of pressure caused by it was also very small. This was measured roughly by its effect on a column of mercury so arranged that after ignition the mercury in both limbs of a U-tube would be level. The mean of three experiments with a 3.9 per cent. mixture gave a momentary

increase of pressure equal to 3 or 4 cm. Mixtures containing more ether gave far greater pressures.

It was found that a 0.3 cm. mesh iron gauze, or a 0.2 cm. mesh brass gauze, prevented the passage of a cool flame down a glass tube 7 cm. in diameter.

Discussion of Results.

The sub-ignition-temperature figures given above agree fairly well with ignition-temperatures previously published for alcohol and acetone. The sub-ignition-temperature given for ether-air mixtures, however, whilst agreeing almost exactly with the ignition-temperature given by Alilaire, differs notably from the other figures available. The difference is probably to be accounted for by the fact that in the methods employed to obtain these, no account was taken of the cool flame of ether: the cool flame of alcohol can only be obtained near the temperature at which an explosion or ordinary combustion occurs directly. This may be justifiable and necessary in the determination of ignition-temperatures, but involves the neglect of a phenomenon which can, and very often does, give rise to ordinary combustion under suitable conditions. Moreover, these conditions are precisely those liable to obtain during solvent-recovery on the manufacturing scale, namely, the presence of a large volume of the solvent-air mixture and some degree of confinement.

That ordinary combustion of a dangerous nature could be caused by heating an ether-air mixture in glass tubes to 187° was proved again and again when using 4 and 5.5 cm. tubes, particularly if the percentage of solvent lay between 5 and 9. That this result was a genuine one was proved by stopping a current of ether in air flowing along a glass tube kept at 187°. Ignition of the ether occurred in every case. The method employed to determine sub-ignition temperatures thus appears to be a practical one, and also has the advantage of being easily adaptable to determine the effect of substituting for glass any material that might be used in manufacture.

The ignition observed by Alilaire must indubitably have commenced as a cool flame. The temperatures necessary to obtain such a flame in mixtures containing fair quantities of ether, as shown by us, are fairly near the temperatures attainable in a steam-heated building, particularly when it is considered that the presence of metals lowers the sub-ignition temperature appreciably. On the other hand, the results previously obtained for the ignition-

temperature of ether-air mixtures are far above those one can conceive of being attained in such a building, except in the most extraordinary circumstances.

The results show that a quiescent gas appears to be more easily ignited than one in motion, but the experimental work covers only a very small range of velocities, and in any case the propagation of flame is more easily and quickly carried out by gas in motion.

The presence of glyceryl trinitrate in a gas-mixture, as was anticipated from its amount, does not seem to affect the temperature of sub-ignition or the limits of propagation of flame. The peroxides sometimes present in ether in very small amounts can, however, affect both its ignition and its propagating qualities if present in sufficient quantity. Our work seems to indicate that their influence in causing primary ignition could only be inappreciable, although it is quite conceivable that they could well affect the change from cool to ordinary flame.

Reduction of pressure appeared to cause a lowering of the sub-ignition-temperature of the mixtures examined, but the effect of pressure alone within the range of variation of atmospheric pressure can scarcely have a practical influence on the ignition of the solvent-air mixtures, as for ether-air, for example, a reduction of pressure of 10 cm. near atmospheric pressure caused a variation in the sub-ignition-temperature of less than 2° .

The only phenomenon that could be expected to reduce the sub-ignition-temperature of ether-alcohol-air and ether-air mixtures below the danger limit is thus that described as shock ignition. With a difference of pressure of less than half an atmosphere, it was possible by this method to ignite a gas-mixture at least 170° below its sub-ignition-temperature, so that it is quite conceivable that the development of sudden differences of pressure on the manufacturing scale might easily be the determining factor in bringing about ignition of the solvent-laden air. Exactly how this is to be brought about can only be conjectured, as our inside knowledge of gas-ignition, particularly as regards this fresh phenomenon, is very limited. The present work has shown how many accidents could happen, but much remains to be done before any sound explanation can be given of such a conflagration as was described in *The Times* of March 28th, 1919, when a bottle of ether exploded in a military hospital at Southage. According to the same report, explosions of bottles of ether are of somewhat frequent occurrence.

The results given in the older work for the limits for propagation of flame in ether-air mixtures are 1.8 per cent. and about 9 per cent., the latter being apparently far out, whilst those for alcohol-air mixtures agree fairly well with our results, particularly

as regards the lower limit. The change from 5 cm. glass to 15 cm. iron tube affects the results for the upper limit for horizontal and upward propagation in ether-air mixtures very materially, the limits becoming well over 20 per cent. in each case, instead of 8 per cent. for horizontal propagation and 16 per cent. for upward propagation. The extreme limits determined for ether-air mixtures are thus 1.73 and 23.30 per cent. The upper limit for propagation in alcohol-air mixtures in 5 cm. glass tubes was found to be 18.95 at 60°. As this figure was well above the highest concentration of alcohol vapour obtainable during normal recovery, there was no point in repeating this in the 15 cm. iron tube. The lower limit of propagation for alcohol-air mixtures was only very slightly altered in the large iron tube, falling from 4.24 per cent. in the 5 cm. glass tube to 4.16 per cent.

The results for the propagation of flame in ether-alcohol-air mixtures obtained during this investigation are distinctly interesting. It is found that Le Chatelier's rule holds for all directions of propagation for the lower limit, and for the upper limit for downward propagation. The rule does not hold for the other two directions of propagation for the upper limit, the discrepancies being very considerable in the case of upward propagation. Wheeler's work on acetone-air mixtures has already been discussed, and it may suffice here to state that the limits given by him are 2.15 and 9.7 per cent., our results being 2.88 and 12.40 per cent. The lower limit of 5 per cent. given by Brunswick is obviously wrong, but the upper-limit figure of 12 per cent. is very near that found by us.

It will be seen that the effect of temperature and pressure on the limits for the propagation of flame in ether-air mixtures is quite material. The influence of the velocity of the gas-current was not examined throughout a sufficient range to enable sound conclusions to be drawn as to its effect under manufacturing conditions, but it is fairly clear that a margin must be allowed for this factor when dealing with the limit results obtained. The presence of 1 per cent. of the peroxides of ether in ether-air mixtures appears to have no appreciable effect on the lower limit for the propagation of flame, and it is by no means likely that there would be sufficient peroxide present under practical conditions to affect the upper limit materially.

Summary.

The soap-bubble method described by McDavid (*loc. cit.*) gave for the ignition-temperature of ether-air mixtures results varying from 859° to 1068°. The method seemed to be untrustworthy.

The other method used seemed to give the minimum temperature at which the reaction in a combustible gas-mixture became self-supporting—called the sub-ignition-temperature. This temperature, which appears to be the one required from a safety point of view, was 187° for ether-air mixtures in glass, and varied from 187° to about 500° for the different ether-alcohol-air mixtures used. It was about 500° for acetone-air mixtures. The presence of appreciable quantities of metal in the vessels used lowered the sub-ignition-temperature.

Decrease of pressure appeared to reduce the sub-ignition-temperature of a mixture, but the presence of small quantities of glyceryl trinitrate or of diethyl peroxide had little effect on the sub-ignition-temperature of ether-air mixtures. The sub-ignition-temperature of such mixtures was lowered by the presence of ethyl hydrogen peroxide. The effect of slight velocities seemed to be to raise the sub-ignition-temperature of ether-air mixtures.

When an exhausted vessel is quickly put into communication with a reservoir containing ether-air or carbon disulphide-air mixtures, under specified conditions the gas can be ignited at the ordinary temperature. This phenomenon has been termed shock ignition.

The limits for the propagation of flame in mixtures of ether-alcohol-air and ether-acetone-air have been determined in 2.5 and 5 cm. tubes of glass and in 5 and 15 cm. tubes of iron. The extreme limits found were 1.73 and 23.30 per cent. for ether-air mixtures, 4.16 and 18.95 per cent. for alcohol-air mixtures, and 2.88 and 12.40 per cent. for acetone-air mixtures. The upper limit for propagation in alcohol-air was determined at 60° . Figures obtained with the 15 cm. iron tube often differed appreciably from those obtained with 5 cm. glass tubes.

Le Chatelier's rule was found to hold fairly well for ether-alcohol-air mixtures, except for horizontal and upward propagation in the case of the upper limit. The only considerable deviation from the rule in the case of ether-acetone-air mixtures was observed for upward propagation and the upper limit.

Increase of temperature was found to raise the upper limit for propagation in ether-air notably, and reduction of pressure was found to narrow the limits. Increase in the velocity of the gas-mixture widened the limits materially. The presence of the peroxides of ether scarcely affected the lower limit of propagation in ether-air, but any considerable quantity raised the upper limit of such a mixture.

It was found impossible to ignite ether-alcohol-air mixtures by means of steel to steel, emery to steel, or pyrites to steel sparks, but

THE CONDUCTIVITIES OF IODOANILINESULPHONIC ACIDS. 1505

inflammation was readily obtained when using ferro-cerium to steel sparks.

Many of the properties of ether-air mixtures appear to be explained by the formation of a cool flame.

Further work is contemplated on the phenomenon referred to as shock ignition.

We desire to express our thanks to Messrs. Nobel's Explosives Co., Ltd., for whom the work was carried out, and particularly to Mr. W. Rintoul, Manager of the Research Section, for kind permission to publish our results. We also wish to thank Mr. A. W. Sanderson for assistance in carrying out some of the experimental work.

THE RESEARCH LABORATORIES,
ARDEER FACTORY, STEVENSTON. [Received, September 22nd, 1919.]

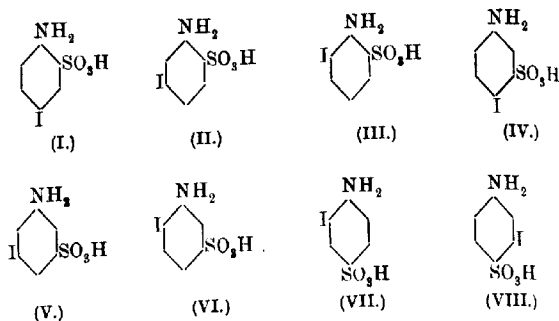
XXXIX.—*The Conductivities of Iodoanilinesulphonic Acids.*

By MARY BOYLE.

No systematic study of the halogen-substituted derivatives of the anilinesulphonic acids seems to have been attempted. Eight out of the ten possible monochloro-, about five of the monobromo-, and three monoiodo-derivatives have been described by P. Fischer, Post, Meyer, Bahlmann, etc., but in some cases the constitution is left uncertain and in most others there is merely a simple statement of the preparation and properties of individuals; owing to the incomplete character of the group, no comparative study of either the chloro-, bromo-, and iodo-substituted derivatives or of the different members of a group of acids substituted by one particular halogen has been possible. It was thought that it might be interesting to study one particular property throughout a complete series, in order to determine how the value of that property is affected by the position in the nucleus taken by the halogen relative to the two other groups present. The series chosen was that of the iodoanilinesulphonic acids, and the property that of electrical conductivity.

So far, however, it has not been found possible to prepare the

ten possible isomerides, but the following eight, of established constitution, are now known:



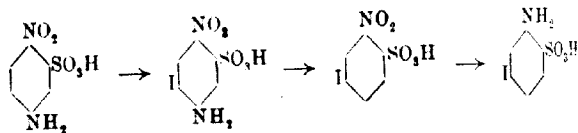
The series of chloroanilinesulphonic acids described by P. Fischer, Meyer, Claus, Goslich, Limpricht, etc., corresponds closely with the above, except that the chloro-analogue of III is unknown, and that a 3-chloroaniline-2-sulphonic acid described by Post and Meyer has no counterpart, up to the present, among the iodine compounds.

2-Iodoaniline-4-sulphonic acid (VII) was described in a patent by Kalle & Co. (D.R.-P. 129808), and its constitution established in 1909.

4-Iodoaniline-2-sulphonic acid (I) and 3-iodoaniline-4-sulphonic acid (VIII) were described by the author in 1909 (T., 95, 1689, 1709).

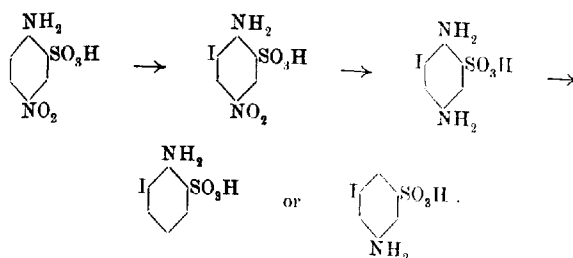
The others have been prepared from various nitroanilinesulphonic acids, as described below.

5-Iodoaniline-2-sulphonic acid (II) was obtained from *p*-nitroaniline-*m*-sulphonic acid by treating it with iodine chloride, removing the amino-group, and subsequently reducing the nitro-group.



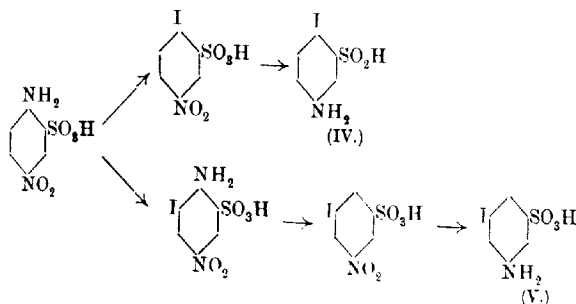
6-Iodoaniline-2-sulphonic acid (III) was prepared with more difficulty, and small quantities only have been obtained. The *p*-nitroaniline-*o*-sulphonic acid described in 1911 (T., 99, 325) gave, when treated with iodine chloride, an iodo-derivative, for which only one configuration is possible. Reduction of the nitro-group gave a diaminosulphonic acid, which, by the loss of one amino-

group, could yield two different iodoanilinesulphonic acids, as figured below:

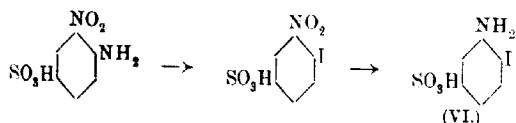


Considerations of steric hindrance would suggest the first as the more probable reaction, and that it does take place exclusively is proved by the conversion of the iodoanilinesulphonic acid into the well-known 2:3-di-iodobenzenesulphonic acid.

4-Iodoaniline-3-sulphonic acid (IV) and 5-iodoaniline-3-sulphonic acid (V) were both obtained from *p*-nitroaniline-*o*-sulphonic acid by submitting it to the following series of reactions:



6-Iodoaniline-3-sulphonic acid (VI) was obtained by a similar series of reactions from *o*-nitroaniline-*p*-sulphonic acid.



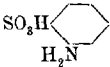
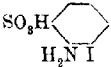
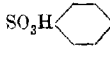
These acids resemble each other in appearance, being well characterised, colourless substances crystallising from water in needles. They vary somewhat in solubility in water, the 6-iodo-

aniline-2-sulphonic acid being readily soluble, most of the others giving $N/32$ — $N/64$ -solutions, and 3-iodoaniline-4-sulphonic acid dissolving sparingly. The latter acid crystallises with one molecule of water; the rest are anhydrous.

In the experiments on conductivities, the main difficulty experienced was in the accurate determination of the strength of the acid solution. The unsubstituted anilinesulphonic acids were first investigated, the pure acids being either (1) weighed out to the required strength, or (2) titrated with standard alkali and diluted to the required strength; the two methods were found to give identical results when special precautions in the standardisation of materials were taken. The numbers obtained in the case of the three anilinesulphonic acids are all higher than the corresponding numbers obtained by Ostwald (*Zeitsch. physikal. Chem.*, 1889, **3**, 106), Winkelblech (*ibid.*, 1901, **36**, 546), White and Jones (*Amer. Chem. J.*, 1909, **42**, 520), and Wheeler and Jones (*ibid.*, 1910, **44**, 159). It is to be noted, however, that these higher values give a better dissociation constant than do the earlier and lower ones. For example, for aniline-*p*-sulphonic acid, Ostwald gives a mean $K = 5.81 \times 10^{-4}$, showing a maximum variation of 0.8×10^{-5} , Winkelblech a mean $K = 6.2 \times 10^{-4}$ with a variation of 2.3×10^{-5} , Wheeler and Jones a mean $K = 6.55 \times 10^{-4}$ and variation 1.7×10^{-5} , and the author a mean $K = 7.05 \times 10^{-4}$ with a variation of 0.6×10^{-5} .

For aniline-*o*-sulphonic acid, the mean value $K = 4.29 \times 10^{-3}$, as against Ostwald's $K = 3.21 \times 10^{-3}$, and for aniline-*m*-sulphonic acid the value $K = 2.11 \times 10^{-4}$, as against Ostwald's $K = 1.85 \times 10^{-4}$ and Wheeler and Jones' $K = 1.97 \times 10^{-4}$, have been obtained.

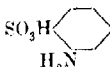
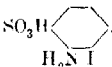
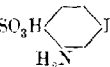
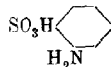
The introduction of iodine into the nucleus increases the conductivities of the acids very considerably, bringing them into the category of strong acids, which do not obey Ostwald's dilution law; in the case of some of the aniline-*m*-sulphonic acids only can a value of K which is even approximately constant be obtained. It is the position of the iodine relative to the amino-group which is the determining factor; whether in the meta- or para-position the effect in increasing the strength of the acid is approximately the same, but when in the ortho-position the effect is very marked. The influence of the amino group in diminishing the strength of the sulphonic acid is almost entirely neutralised by the ortho-substituted iodine, and the iodoamino sulphonic acid is found to conduct to the same extent as benzenesulphonic acid itself. A comparison of 6-iodoaniline-2-sulphonic acid with aniline-*o*-sulphonic acid and with benzenesulphonic acid shows this clearly.

			
ν .	λ_{ν} .	λ_{ν} .	λ_{ν} .
32	109.5	—	321.07
64	144.1	340.0	—
128	183.4	348.2	350.47
256	225.8	353.1	—
512	265.0	356.7	356.38
1024	299.5	357.8	359.03
2048	—	—	354.22

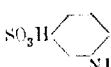
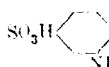
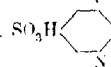
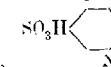
The figures for benzenesulphonic acid are those given by Wightman and Jones (*Amer. Chem. J.*, 1911, **46**, 56).

The three following tables give the conductivities of the iodo-substituted acids side by side with those of the unsubstituted acid from which they are derived.

Aniline-o-sulphonic Acid,




				
ν .	λ_{ν} .	λ_{ν} .	λ_{ν} .	λ_{ν} .
32	109.5	—	—	—
64	144.1	340.0	—	—
128	183.4	348.2	309.5	289.6
256	225.8	353.1	333.2	320.9
512	265.0	356.7	348.7	341.6
1024	299.5	357.8	357.4	355.0

Aniline-m-sulphonic Acid,

						
ν .	λ_{ν} .	λ_{ν} .	λ_{ν} .	$K \times 10^4$.	λ_{ν} .	$K \times 10^4$.
32	28.15	—	—	—	—	—
64	39.12	242.3	115.3	23.5	73.98	8.30
128	54.01	286.4	149.5	23.0	99.14	8.15
256	73.98	319.3	191.2	23.5	130.2	8.02
512	99.28	342.2	235.5	24.1	167.8	7.94
1024	131.5	358.2	279.0	—	210.4	8.00
	$K =$		$K =$		$K =$	
	2.11×10^{-4} .		23.5×10^{-4} .		8.08×10^{-4} .	

Ostwald's value $\lambda_{\nu} = 356$ has been used in calculating the dissociation constants of the anilinesulphonic acids, and $\lambda_{\nu} = 360$ for calculating those of the iodoanilinesulphonic acids.



Aniline-p-sulphonic Acid.



SO_3H  NH_2 SO_3H  NH_2 SO_3H  NH_2			
<i>v.</i>	$\lambda_{\text{p.}}$	$\lambda_{\text{p.}}$	$\lambda_{\text{p.}}$
32	49.73	266.7	—
64	68.30	301.9	—
128	92.54	329.5	—
256	122.9	347.4	228.7
512	159.4	360.0	268.4
1024	200.7	366.2	302.7

The same screening of the amino-group is brought about by other groups than iodine, for example, bromine, the nitro-group, hydroxy-group, etc., although none is quite so effective as iodine. From the literature on the subject of conductivities of acids, the following data have been selected as bearing out what has been shown to be true of iodo-substituted acids.

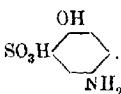
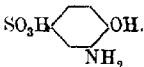
Bromo-derivatives of Anilinesulphonic Acids.

The acid containing bromine in the ortho-position with respect to the amino-group has a greater conductivity at all dilutions than the one with bromine in the para-position.

SO_3H  NH_2 SO_3H  NH_2			
<i>v.</i>	$\lambda_{\text{p.}}$	$\lambda_{\text{p.}}$	$\lambda_{\text{p.}}$
64.0	70.0	—	—
73.5	—	—	224.4
128.0	92.3	—	—
147.0	—	—	351.8
256.0	122.5	—	—
294.0	—	—	276.5
512.0	157.4	—	—
588.0	—	—	296.3
1024.0	197.5	—	—
1176.0	—	—	312.6

SO_3H  H_2N SO_3H  H_2N			
<i>v.</i>	$\lambda_{\text{p.}}$	$\lambda_{\text{p.}}$	$\lambda_{\text{p.}}$
109.8	—	—	338
219.6	—	—	343
278.0	338	—	—
439.2	—	—	346
556.0	346	—	—
878.4	—	—	348
1112.0	351	—	—

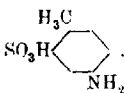
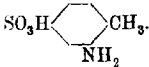
Hydroxy-derivatives of Anilinesulphonic Acids.

		
ν .	λ_{cr}	λ_{cr}
64	—	26.5
128	—	36.9
256	16.0	51.0
512	22.4	69.8
1024	31.3	125.0

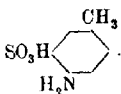
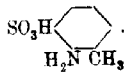
Here the same thing is observed, although both acids have a smaller conductivity than the unsubstituted metanilic acid.

Alkyl Derivatives of Anilinesulphonic Acids.

The introduction of methyl into aniline-*m*-sulphonic acid gives results in harmony with the above.

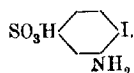
		
ν .	λ_{cr}	λ_{cr}
32	12.6	—
64	17.7	42.3
128	24.7	56.8
256	34.5	77.2
512	47.7	104.6
1024	—	137.5

In the case of aniline-*o*-sulphonic acid, however, the position of the substituted group in the nucleus seems to make practically no difference to the conductivity value.

		
	λ_{cr}	λ_{cr}
32	53.0	51.0
64	73.7	69.9
128	99.5	94.6
256	131.4	125.2
512	169.1	162.5
1024	210.9	—

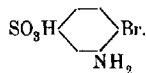
Halogen Derivatives of Anilinesulphonic Acids.

Iodine is more effective than bromine in neutralising the effect of the amino-group, and bromine than chlorine. This is seen from a consideration of the three following tables:

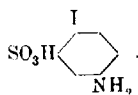


ν ,
64.0
73.5
128.0
147.0
256.0
294.0
512.0
588.0
1024.0
1176.0

λ_{m} ,
243.3
—
286.4
—
319.3
—
342.2
—
358.2
—

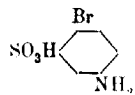


λ_{m} ,
—
224.4
—
[251.8
—
276.5
—
296.3
—
312.6

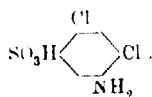


ν ,
64.0
128.0
256.0
512.0
1024.0

λ_{m} ,
73.98
99.14
130.2
167.8
210.4

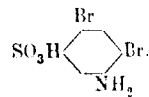


λ_{m} ,
70.0
92.3
122.5
157.4
197.5



ν ,
64.0
71.9
128.0
143.8
256.0
287.6
512.0
575.2
1024.0
1150.0
2048.0

λ_{m} ,
—
—
130.0
—
158.4
—
189.2
—
227.9
—
268.5



λ_{m} ,
—
262
—
289
—
313
—
329
—
340
—

EXPERIMENTAL.

Preparation of the Acids.

4-Iodoaniline-2-sulphonic acid was prepared from aniline-*o*-sulphonic acid according to the method previously described (T., 1909, **95**, 1698). After repeated crystallisations, the acid still possessed a faint violet tinge (Found: C=24.03; H=1.99. Calc.: C=24.07; H=2.00 per cent.).

Solubility.—One hundred grams of water dissolve 0.51 gram of the acid at 25°.

5-Iodoaniline-2-sulphonic Acid.—The method of preparation consists in (a) introducing iodine into *p*-nitroaniline-*m*-sulphonic acid, (b) displacing the amino-group by hydrogen, (c) reducing the nitro-group.

(a) *Preparation of 6-Iodo-4-nitroaniline-2-sulphonic Acid.*—Fifteen grams of 4-nitroaniline-3-sulphonic acid, prepared by Eger's method from aniline-*m*-sulphonic acid (Ber., 1888, **21**, 2581), were dissolved in a large volume of boiling water, a little hydrochloric acid was added, and 11.2 grams of iodine chloride were then passed into the solution, which was kept at 90–95°. Experiments were carried out at lower temperatures, but the sparing solubility of the acid enabled only small quantities to be worked up at a time, and the yield was only inappreciably increased. The reddish-yellow solution, after remaining for half an hour, was evaporated to a very small bulk, when the dark yellow acid separated on cooling. A yield of 20.4 grams, amounting to 87 per cent. of the theoretical, was obtained.

(b) *Preparation of 4-Iodo-2-nitrobenzenesulphonic Acid.*—Fifteen grams of the above acid were diazotised in sulphuric acid solution by means of 3 grams of sodium nitrite. The sparingly soluble diazo-compound was then boiled with alcohol under a reflux condenser, and the dark-coloured residue, after removing the alcohol, was dissolved in water, neutralised with sodium carbonate and boiled with animal charcoal; the yellow filtrate deposited, on concentration, long yellow needles, which became opaque on exposure to air. The yield amounted to nearly 70 per cent. of the theoretical.

(c) *Preparation of 5-Iodoaniline-2-sulphonic Acid.*—The nitro-acid was reduced, as usual, with stannous chloride at 100°. There was little apparent action, the solution retaining its yellow colour, but when the yellow solid which was precipitated on cooling was dissolved in sodium carbonate, a white amino-acid was obtained

from this solution by adding concentrated acid. Proof of its structure was obtained by replacing the amino-group by iodine and converting the di-iodobenzenesulphonic acid into a chloride melting at 75° , and identical with 2:4-di-iodobenzenesulphonyl chloride:

0.1341 gave 0.1181 CO_2 and 0.0248 H_2O . $\text{C}=24.01$; $\text{H}=2.05$.
 $\text{C}_6\text{H}_4\text{O}_3\text{NIS}$ requires $\text{C}=24.07$; $\text{H}=2.00$ per cent.

Solubility.—One hundred grams of water contain 0.26 gram of acid at 25° .

6-Iodoaniline-2-sulphonic Acid.—6-Iodo-4-nitroaniline-2-sulphonic acid (T., 1911, **99**, 330) was reduced with stannous chloride at 100° to 6-iodo-*p*-phenylenediamine-2-sulphonic acid, which is a white, crystalline substance sparingly soluble in water. A small quantity (2.5 grams) was diazotised in the minimum amount of sulphuric acid by adding 0.55 gram of sodium nitrite (theoretical amount for one amino-group is 0.53 gram); the dark yellow diazo-compound was then collected and boiled with alcohol. After evaporating off the alcohol and boiling the neutralised residue with animal charcoal, the filtered solution and the amino-acid precipitated from it were still somewhat coloured. This amino-acid has not yet been obtained in a colourless condition; it crystallises in pale brown needles from water, in which it is rather readily soluble. Its conversion into 2:3-di-iodobenzenesulphonyl chloride, melting at 127° , confirmed its constitution:

0.1937 gave 0.1701 CO_2 and 0.0370 H_2O . $\text{C}=23.95$; $\text{H}=2.11$.
 $\text{C}_6\text{H}_4\text{O}_3\text{NIS}$ requires $\text{C}=24.07$; $\text{H}=2.00$ per cent.

4-Iodoaniline-3-sulphonic Acid.—Nineteen grams of *p*-nitroaniline-*o*-sulphonic acid (T., 1911, **99**, 324) were diazotised in sulphuric acid solution by 5.7 grams of sodium nitrite, and the bright yellow diazo-compound was decomposed by potassium iodide. A voluminous yellow precipitate of potassium 2-iodo-5-nitrobenzenesulphonate separated at once from the hot solution, and was collected and well washed with cold water. This salt was suspended in concentrated hydrochloric acid and reduced with stannous chloride, the completion of the reduction being readily ascertained by the change in colour and in the appearance of the crystalline product. The amino-acid was purified, as usual, by precipitating it with concentrated acid from its solution in sodium carbonate. It separates from a concentrated aqueous solution in small, sparkling crystals, from more dilute solutions in fine, transparent needles. Its conversion into 2:5-di-iodobenzenesulphonyl chloride, melting at 132° , afforded proof of its constitution:

0.1871 gave 0.1644 CO_2 and 0.0331 H_2O . $\text{C}=23.96$; $\text{H}=1.97$.
 $\text{C}_6\text{H}_6\text{O}_3\text{NIS}$ requires $\text{C}=24.07$; $\text{H}=2.00$ per cent.

Solubility.—One hundred grams of water contain 1.36 grams of anhydrous acid at 25° .

5-Iodoaniline-3-sulphonic acid was prepared from *p*-nitroaniline-*o*-sulphonic acid through 6-iodo-4-nitroaniline-2-sulphonic acid by (1) removing the amino-group, (2) reducing the nitro-group. When the diazo-compound was boiled with alcohol, nitrogen was evolved rapidly, and, after about forty-five minutes, a clear, pale yellow solution was obtained, from which, on concentration, pale yellow crystals separated; these were neutralised with sodium carbonate, and the sodium salt was recrystallised. Sodium 3-iodo-5-nitrobenzenesulphonate was dissolved in hydrochloric acid and reduced with stannous chloride at 100° ; precipitation of the amino-acid as a cream-coloured, crystalline mass followed almost immediately. The acid, dissolved in alkali and reprecipitated by mineral acid, was then repeatedly crystallised from hot water, separating in fine, white needles:

0.1778 gave 0.1569 CO_2 and 0.0326 H_2O . $\text{C}=24.07$; $\text{H}=2.03$.
 $\text{C}_6\text{H}_6\text{O}_3\text{NIS}$ requires $\text{C}=24.07$; $\text{H}=2.00$ per cent.

Solubility.—One hundred grams of water dissolve 1.31 grams of anhydrous acid at 25° .

The constitution of the acid was established by replacing the amino-group by iodine and converting the resulting di-iodobenzene-sulphonic acid into 3:5-di-iodobenzene-sulphonyl chloride, which crystallised from ether in needles melting at 93° .

6-Iodoaniline-3-sulphonic Acid.---*o*-Nitroaniline-*p*-sulphonic acid was prepared (1) by nitrating sulphanilic acid according to Nietzki's method (*Ber.*, 1885, **18**, 294). (2) by sulphonating *o*-nitroaniline by Hardtung's method (*Annalen*, 1881, **206**, 96). After displacing the amino-group by iodine, and subsequently reducing the nitro-group, the iodoaminosulphonic acid was obtained as a grey powder, which crystallised from a large bulk of water:

0.2075 gave 0.1833 CO_2 and 0.0388 H_2O . $\text{C}=24.09$; $\text{H}=2.07$.
 $\text{C}_6\text{H}_6\text{O}_3\text{NIS}$ requires $\text{C}=24.07$; $\text{H}=2.00$ per cent.

Solubility.—One hundred grams of water contain 0.48 gram of acid at 25° .

2-Iodoaniline-4-sulphonic acid was prepared as previously described (T., 1909, **95**, 1693) (Found: $\text{C}=24.03$; $\text{H}=2.11$. Calc.: $\text{C}=24.07$; $\text{H}=2.00$ per cent.).

Solubility.—One hundred grams of water dissolve 2.07 grams of the anhydrous acid at 25°.

3-Iodoaniline-4-sulphonic acid was prepared by reducing 2-iodo-4-nitrobenzenesulphonic acid (T., 1909, 95, 1708) by means of stannous chloride. The reduction proceeded rapidly on the water-bath, and was complete in less than an hour. The iodoamino-acid, precipitated from its solution in alkali by concentrated mineral acid, was recrystallised from water several times, separating in fine, transparent needles containing one molecule of water of crystallisation:

0.1861 gave 0.1552 CO₂ and 0.0425 H₂O. C=22.74; H=2.53.

C₆H₄O₃NIS.H₂O requires C=22.71; H=2.52 per cent.

Solubility.—One hundred grams of water dissolve 0.194 gram of anhydrous acid at 25°.

Conductivity experiments were carried out in Ostwald cells in a thermostat at 25°. An ordinary Wheatstone bridge, carefully calibrated, and standard resistances were employed. The conductivity water was obtained by distilling first with acid, then with alkaline permanganate, finally alone, in the ordinary form of apparatus, consisting of tin distilling flask, block-tin condenser, and Jena-glass receiver. In making the solution of the acid for conductivity measurements, excess of the acid was shaken vigorously in a Jena-glass flask with conductivity water and allowed to remain for some time. The solid was then filtered off and the filtrate titrated against standard sodium hydroxide of slightly less strength; the solution was then diluted to that strength. Standard flasks, pipettes, and burettes were used throughout.

In the preparation of the standard solutions, conductivity water was used throughout. *N*/10-Sodium hydroxide was titrated against *N*/10-hydrochloric acid which had previously been standardised by means of pure sodium carbonate, and each solution was then diluted to *N*/32, *N*/64, *N*/128, *N*/256, and titrations of one against the other were carried out in order that errors introduced by the hydrolysis of the indicator, phenolphthalein, at such considerable dilutions should be obviated. The results of experiments carried out under these conditions agreed well with those obtained by weighing out the acid directly and dissolving it in the requisite amount of water. After one set of results had been obtained, the acid was recrystallised and the conductivity again determined; the recrystallisations and subsequent determination of conductivity were repeated until consecutive experiments gave identical results; in this way, the purity of the acid was guaranteed. In some cases,

ten crystallisations had to be carried through before satisfactorily concordant results were obtained.

Further experiments on the conductivities of the anilinesulphonic acids are being carried out, and it is hoped that the results may shortly be ready for publication.

I wish to express my thanks to Miss E. E. Field for valuable help given during the course of this investigation.

ROYAL HOLLOWAY COLLEGE,
ENGLEFIELD GREEN,
SURREY.

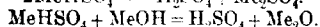
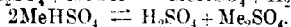
[Received, October 8th, 1919.]

Organic Chemistry.

Chlorination of Methane. J. PFEIFER, F. MAUTHNER, and O. REITLINGER (*J. pr. Chem.*, 1919, [ii], **99**, 239—242).—The process has been studied by passing suitable mixtures of chlorine and a natural gas consisting of nearly pure methane, free from ethylene hydrocarbons but containing small amounts of nitrogen and oxygen, over antimony pentachloride or ferric chloride contained in a quartz tube heated at 360—400°. With the former catalyst and the gases mixed in the proportion of one volume of methane to two volumes of chlorine, methylene chloride (5·8%), chloroform (20·3%), carbon tetrachloride (5·9%), and hydrogen chloride (32%) were obtained, 64% of the chlorine entering into action. With ferric chloride and equal volumes of the two gases, the substances formed were methyl chloride (5·8%), methylene chloride (15·7%), chloroform (21·7%), and hydrogen chloride (43·2%), 86·4% of the chlorine being used; when 2 volumes of chlorine were employed for each volume of methane, there were obtained methyl chloride (traces), methylene chloride (13·25%), chloroform (22·2%), carbon tetrachloride (6·35%), and hydrogen chloride (41·8%), 83·6% of the chlorine entering into action. With 2 volumes of methane to 1 volume of chlorine, 30·1% of methyl chloride and a mixture of approximately equal amounts of methylene chloride and chloroform were produced. When the proportion of methane to chlorine was 3:1, the yield of methyl chloride rose to 40% of that theoretically possible. Attempts to secure carbon tetrachloride in good yield by increasing the relative amount of chlorine were rendered difficult by the occurrence of violent explosions; a mixture of chloroform and carbon tetrachloride was, however, obtained by the use of methane (1 vol.) and chlorine (3 vols.) diluted with nitrogen (2 vols.).
H. W.

Action of Concentrated Sulphuric Acid on Methyl Alcohol.

J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, **169**, 655—657).—The yield of methyl sulphate in the action of sulphuric acid on methyl alcohol increases steadily as the molecular proportion of the sulphuric acid in the reacting mixture increases. The complete mechanism of the reaction is given by the three equations:



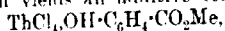
The combined equilibrium of the first two reactions is, to a large extent, independent of the temperature, but the velocity with which the equilibrium is reached is largely influenced by the temperature.

W. G.

Action of Sulphuric Anhydride and of Fuming Sulphuric Acid on Methyl Alcohol. Preparation of Methyl Sulphate.

J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, 164, 795—797).—By the action of 60% fuming sulphuric acid on pure methyl alcohol in the calculated proportion, methyl sulphate may readily be obtained, the yield exceeding 90%. An alternative method is to pass the vapour of methyl ether into the acid until the whole of the sulphuric anhydride, which it contains, is converted into methyl sulphate, and then to distil the mixture. [See, further, *J. Soc. Chem. Ind.*, 1919, 924A.] W. G.

Compounds of Thorium. I. Addition and Substitution Compounds of Thorium Chloride. G. JANTSCH and W. URBACH (*Helv. Chim. Acta*, 1919, 2, 490—500).—Thorium chloride on boiling with absolute alcohol forms a white, very deliquescent additive compound, $\text{ThCl}_4 \cdot 4\text{EtOH}$; this crystallises in fine, prismatic plates, and slowly loses alcohol on keeping. On shaking anhydrous thorium chloride with acetone, solution occurs after a short time, and on keeping over phosphoric oxide the additive compound, $\text{ThCl}_4 \cdot 2\text{COMe}$, separates in small, white, prismatic needles. Heating thorium chloride with acetophenone in chloroform solution gives a clear solution which on keeping over phosphoric oxide yields long, white needles of $\text{ThCl}_4 \cdot 4\text{COPhMe}$, which are very hygroscopic and lose the whole of their acetophenone on keeping. A similar compound, $\text{ThCl}_4 \cdot 4\text{COPh}$, is produced when benzophenone is substituted for acetophenone in the last preparation. Thorium acetate is prepared as a white, crystalline mass by heating anhydrous thorium chloride with anhydrous acetic acid. Thorium benzoate is prepared as a white, crystalline precipitate by heating benzoic acid in xylene solution with anhydrous thorium chloride as long as hydrogen chloride is evolved. If, however, the reaction takes place in light petroleum of high boiling point the chlorobenzoate is produced. This compound, $\text{ThCl}(\text{OBz})_3$, is very hygroscopic, and is quite insoluble in benzene and chloroform. When thorium chloride is heated with four molecules of salicylaldehyde in ethereal solution a clear, yellow solution is produced, from which on further heating separates a light yellow, crystalline, additive compound, $\text{ThCl}_4 \cdot 2\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$. If, however, the ether is replaced by chloroform, the substitution product, $\text{ThCl}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO})_2$, is formed as a canary-yellow, crystalline precipitate, which is very hygroscopic. Thorium chloride heated with three molecules of methyl salicylate in ethereal suspension yields an additive compound,



in fine, white needles; if chloroform, benzene, or xylene is substituted for ether, three substitution products are obtained, depending on the amount of ester employed, (1) with 2 molecules of ester in chloroform the compound $\text{ThCl}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$ is formed in fine, white needles; (2) with 4 molecules of ester in benzene the compound $\text{ThCl}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me})_2$ is formed in white needles; (3) with 6 molecules of ester in xylene a faintly yellow substance,

$\text{ThCl}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me})_3$, is obtained, which on washing with light petroleum becomes white.

J. F. S.

Ethylene Chlorohydrin and $\beta\beta'$ -Dichloroethyl Sulphide.

M. GOMBERG (*J. Amer. Chem. Soc.*, 1919, **41**, 1414—1431).—An account of work done under the auspices of the American Bureau of Mines, War Gas Investigations. Many of the conclusions are already well known, but they may be summarised as follows.

I. Preparation of Ethylene Chlorohydrin.—In analogy to the reactions between bromine water and ethylene discussed by Read and Williams (T., 1917, **111**, 240), the author expected that the controlling factors would be the velocities of the reactions between ethylene and chlorine or hypochlorous acid, and actually found that by passing the two gases into water, keeping ethylene in slight excess, a concentration of 6—8% of chlorohydrin is reached before an appreciable amount of dichloride is formed. Up to this point the gases are absorbed rapidly at 10—12° (about 20—25 litres of each per hour in the experiments), but thereafter the reaction becomes sluggish. With a slow stream of gas, however, concentrations of chlorohydrin as high as 14—15% may be reached, but always accompanied by much dichloride. The influence of dissolved chlorohydrin, hydrogen chloride, or metallic chlorides on the course of the reaction was roughly determined. Chlorohydrin itself is rather helpful at the outset, and hydrochloric acid up to 2*N*- is no hindrance to the exclusive production of the chlorohydrin. The combined effect, however, is more important, for when both are present in *N*-concentration, the formation of ethylene dichloride is favoured. Metallic salts are much more harmful, and consequently any attempt to neutralise the hydrochloric acid formed during the reaction $[\text{H}_2\text{O} + \text{Cl}_2 \rightleftharpoons \text{HClO} + \text{HCl}]$ does more harm than good. Efficient stirring is obviously most important. Altogether, it is not advisable to aim at more than 8% concentrations of chlorohydrin. The refractive index gives a measure of the concentration (water, 1.333; chlorohydrin, 1.442).

II. Concentration and Isolation of the Chlorohydrin.—A 42.5% solution of chlorohydrin in water has the constant boiling point 95.8°. More dilute solutions can therefore be enriched by distillation, and entirely freed from hydrochloric acid. The effect of salts on the course of the distillation is striking. For example, 9 litres of a 7.3% solution were neutralised with lime and distilled, 4 litres being collected; this was saturated with salt and distilled again, 1.6 litres being collected; this was saturated with calcium chloride and concentrated by distillation to 1 litre, the resulting solution containing nearly all the original chlorohydrin, being 64%. The subject of "salting out" the chlorohydrin appears to offer many interesting problems. Saturation with sodium sulphate at 32—33° seems to offer the best results: the aqueous layer is about 7% chlorohydrin, whilst the separated oil contains about 68% of chlorohydrin and only about 0.65 gram of sodium sulphate per 100 c.c. A combination of distillation, "salting out," and extraction with ether, benzene, or perhaps ethylene dichloride would be the best scheme

for isolating the pure compound. Very little hydrolysis takes place during the distillations.

III. *Conversion into $\beta\beta'$ -Dichloroethyl Sulphide*.—The reaction with sodium sulphide proceeds just as well with 20% solutions of chlorohydrin as with more concentrated solutions, and only a small excess of the salt is required. Concentration being necessary at some point, however, it is best to use 40–80% solutions. After the reaction, which is completed by warming, the solution is neutralised by sulphuric acid and evaporated under reduced pressure, when the thiodiglycol, $S(CH_2 \cdot CH_2 \cdot OH)_2$, may be extracted by alcohol. If the isolation of this is not required, however, 70–80% chlorohydrin is added to solid sodium sulphide, the product is neutralised by 90% sulphuric acid, and then mixed with concentrated hydrochloric acid. The salts are filtered and the solution warmed at 60–75°, when the "mustard gas" separates as an oil almost dry and free from hydrogen chloride, the yield being 90–98%.

In an attempt to prepare $\beta\beta'$ -dichloroethyl sulphide by the inter-action of ethylene dichloride and metallic sulphides, it was soon realised that the desired product was more reactive than the parent substance, a disulphide, $(C_2H_4)_2S_2$, being formed when "mustard gas" is even left with sodium sulphide solution in the cold.

J. C. W.

Superalite [Trichloromethyl Chloroformate]. H. P. HOON and H. R. MURDOCK (*J. Physical Chem.*, 1919, 23, 498–512).—The preparation, properties, and decomposition of trichloromethyl chloroformate have been studied. The best method of preparation consists in treating methyl alcohol with carbonyl chloride and chlorinating the product, methyl chloroformate, in bright light with elevation of temperature as the chlorination proceeds. Attempts to prepare this compound directly from carbonyl chloride, or from carbon dioxide and carbon tetrachloride, failed. Trichloromethyl chloroformate is decomposed by charcoal and by ferric oxide into carbonyl chloride. When working in sealed tubes at constant temperature the reaction can be brought to a standstill at any desired point in the presence of iron oxide. Alumina decomposes superalite into carbon tetrachloride and carbon dioxide. Perchlorodimethyl carbonate breaks up on heating into superalite and carbonyl chloride. When methyl chloroformate is chlorinated in light at suitable temperatures the products are chloromethyl chloroformate (b. p. 107°), dichloromethyl chloroformate (b. p. 114°), and trichloromethyl chloroformate (b. p. 128°). When methyl carbonate is chlorinated, the successive products are monochloromethyl carbonate, b. p. 138°, dichloromethyl carbonate, b. p. 178°, and hexachloromethyl carbonate, m. p. 78°. J. F. S.

The Catalytic Reduction of Halogenated Acetic Esters. PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1919, 169, 758–761).—The halogenated acetic esters may readily be reduced to the corresponding acetic esters by passing their vapours along with hydrogen over reduced nickel at 300°. This method has been

successfully applied to ethyl mono-, di-, and tri-chloroacetates and ethyl bromoacetate, good yields of ethyl acetate being obtained. In the case of the di- and tri-chloroacetates, the removal of the chlorine takes place in successive stages. In each case small amounts of ethylene and acetaldehyde are obtained, due to secondary decomposition of the ethyl acetate.

W. G.

[Preparation of] Acetic Anhydride and Paracetaldehyde from Ethylidene Diacetate. J. KOETSCHET and M. BEUDET (U.S. Pat. 1306963).—A mixture of ethylidene diacetate (400 parts) with sulphuric acid (D 1.87) (8 parts) is heated at 70–80° at a pressure of about 100 mm. In two hours 350 parts of a mixture of paracetaldehyde and acetic anhydride distil, and a residue comprising sulphuric acid and 50 parts of unchanged ethylidene diacetate remains in the reaction vessel. To this 350 parts of ethylidene diacetate may then be added and the reaction continued as before. Distillation is facilitated by passing a current of pure or diluted oxygen into the mixture. The formation of the tarry by-products obtained when higher temperatures are employed in effecting the operation at atmospheric pressure is prevented by conducting the reaction in a vacuum.

CHEMICAL ABSTRACTS.

[Preparation of] Ethylidene Diacetate. J. KOETSCHET and M. BEUDET (U.S. Pat., 1306964). Mercuric oxide (40 parts) is dissolved in acetic acid (800 parts), the temperature raised to 70°, and a hot solution of β -naphthalenesulphonic acid in acetic acid (200 parts) is added slowly with stirring. A white precipitate of mercuric naphthalenesulphonate is formed. Acetylene is passed into this mixture at 70°, 200 parts being absorbed during two hours. The ethylidene diacetate formed is then separated from the excess of acetic acid. According to a modification of the procedure, mercuric oxide (40 parts) is dissolved in glacial acetic acid (1000 parts) heated at 70°, and into this solution is run a mixture of sulphoacetic acid (26 parts) and acetic acid (100 parts). On passing acetylene into the resulting mixture, 230 parts of acetylene are absorbed in five hours at 65°. The use of mercuric acetate together with aromatic or aliphatic sulphonic acids, instead of mercuric sulphate, as catalyst enables the reaction to be carried out at lower temperatures without deposition of tarry by-products such as are produced when mercuric sulphate is used and the reaction is effected at 90°.

CHEMICAL ABSTRACTS.

The Distillation of Sodium Stearate and Oleate under Reduced Pressure, and the Origin of Petroleum. AMÉ PICTET and JACQUES POTOK (*Helv. Chim. Acta*, 1919, 2, 501–510).—By the distillation of one kilo. of sodium stearate in ten portions, under 12–15 mm., 700 grams of a pasty mass of hydrocarbons are obtained, leaving 200 grams of a residue which contains very little carbon, or salts of the lower fatty acids, being almost entirely sodium carbonate. The distillate consists chiefly of decane, b. p. 172–175°, tetradecane, b. p. 235–238°, pentadecane, b. p.

257—260°, with tetratriacontane, b. p. above 360°, m. p. 73.5°, as the main constituent, and obviously the primary product. No unsaturated or cyclic hydrocarbons are present. The physical properties of the four hydrocarbons agree with the data assigned by Mabery to specimens isolated from Pennsylvanian petroleum. Dry sodium oleate also gives a 70% yield of oil under these conditions, but all the fractions are ethylenic. The chief hydrocarbons found are nonylene, b. p. 145—148°, decylene, b. p. 160—163°, D_4^{20} 0.7630, n_D^{20} 1.4301, undecylene, b. p. 195—198°, and tridecylene, b. p. 228—231°, agreeing in physical properties with the olefines isolated by Coates and Mabery from American petroleum. No naphthenes are present.

The results therefore confirm Engler's hypothesis, in so far as the open-chain hydrocarbons are concerned, namely, that they originate from the fats of marine plants and animals. As the conditions of the decompositions now effected are about as mild as they could very well be, the absence of any traces of cyclic hydrocarbons, especially optically active naphthenes, would strongly suggest a totally different origin for such substances in natural petroleum, and the authors regard the resins and terpenes as the source.

J. C. W.

The Direct Replacement of Glycerol in Fats by Higher Polyhydric Alcohols. I. Interaction of Olein and Stearin with Mannitol. ARTHUR LAPWORTH and LEONORE KLETZ PEARSON (*Biochem. J.*, 1919, **13**, 296—300).—Glycerol can be quantitatively replaced by mannitol in fats by heating the fat with mannitol in the presence of sodium ethoxide under reduced pressure. An almost theoretical yield of glycerol is obtained in the distillate, whilst the residue in the distillation flask may be treated so as to obtain a synthetic mannitol fat. The maximum yield of glycerol is obtained when the proportion is two molecules of fat to three of mannitol. The mannitol compounds formed appear to be mixtures of dioleates (or di-stearates) of mannitan or *isumannide*.

J. C. D.

The Walden Inversion. P. KARRER and W. KAASE (*Helv. Chim. Acta*, 1919, **2**, 436—454).—Various reactions in the glutaric acid series have been studied, with particular reference to the measurement of the rotations of the products for light of different wave-lengths, from about 656 μ to 461 μ . When the rotations for sodium light only are examined, a fairly regular, but meaningless, fluctuation from *d*- to *l*- is observed, but when the rotation-dispersion curves are considered, a completely different conception of the changes may be formed. Thus, of all the following compounds, formed in the order named, and given the sign of rotation for sodium light, namely, *d*-glutamic acid, *l*- α -chloroglutaric acid, zinc *d*- α -hydroxyglutarate, *l*- α -hydroxyglutaric acid, *d*-butyrolactone- γ -carboxylic acid, and also the ethyl *l*-pyroglutamate formed from the initial acid and the *d*-silver salt of the butyrolactone- γ -carboxylic acid obtained from the *l*-chloroglutaric acid, the only product which gives higher negative rotations the shorter the wave-length,

is the α -chloroglutaric acid. All the others give rotation-dispersion curves which tend to rise to highest points in the positive field. It appears, therefore, that only in the replacements of the amino-group by halogen, and this by hydroxyl, are there any changes in configuration, which is, of course, plausible, for these are the only changes directly affecting the asymmetric carbon atom. The authors go so far as to suggest that the symbol *d*- should be given to those compounds which tend to give positive maxima for their rotations, and *l*- to those which give negative maxima.

To a certain extent, the results and views expressed agree with those of Clough (T., 1918, 113, 526). In one particular, however, there is contradiction. Clough states that phosphorus pentachloride and thionyl chloride produce from α -hydroxy-aliphatic acids chloro-acids of the same configuration, whereas nitrosyl chloride acting on α -amino-acids gives chloro-acids of opposite sign, and the exchange of halogen by hydroxyl, with silver oxide, is accompanied by another change of sign. If both statements are true, a *l*-chloro-acid should give a *d*-hydroxy-acid, and this a *d*-chloro-acid, but in the present case it is found that *l*- α -chloroglutaric acid may be converted into the *d*-hydroxy-acid and this reconverted into the *l*- α -chloro-acid by phosphorus pentachloride.

Similar regularities in their rotation-dispersion curves are shown by aspartic acid and its derivatives. The rotations of the so-called *l*-aspartic acid, its ester and the so-called *l*-malic acid obtained indirectly from it tend to a positive maximum, whereas the *l*-chlorosuccinic acid intermediate between the aspartic and malic acids tends to a negative maximum. Therefore, *l*-aspartic and *l*-malic acids should be called *d*-acids. The rotation of malic acid is difficult to judge, for it depends so much on concentration. The authors have chosen 25% solutions as the maximum concentration for which the curve is normal, but it is obvious that if the direction of the rotation-dispersion curve is to be a test of the configuration, the conditions of solvent, concentration, and temperature must be so chosen that the curve is as characteristic as possible for the compound under examination.

The following table gives the specific rotations at 14° for the

Substance.	C.	D.	Hg.	F.
New designation	656.3	589.3	546.3	486.1 μ
<i>d</i> -Glutamic acid	+8.05°	+10.52°	+12.96°	+17.53°
Ethyl <i>d</i> -pyroglutamate	+3.40	+2.68	+1.59	+1.99
<i>l</i> - α -Chloroglutaric acid	-18.26	-22.67	-26.81	-34.67
<i>d</i> - α -Hydroxyglutaric acid	+2.00	+1.34	+0.67	+0.67
Silver <i>d</i> -butyrolactone- γ -carb- oxylate	+5.67	+8.59	+9.14	+13.16
* <i>d</i> -Butyrolactone- γ -carboxylic acid	+1.11	+2.14	+2.83	+3.66
†	+0.33	+2.67	+3.33	+4.17
‡Zinc <i>d</i> -''-hydroxyglutarate.....	+4.24	+6.65	+8.24	—
§ <i>d</i> -Aspartic acid.....	+3.54	+2.48	+2.13	—
Ethyl <i>d</i> -aspartate	+0.98	+1.73	+2.25	+3.38
<i>l</i> -Chlorosuccinic acid	-15.04	-18.92	-22.96	-30.90

* From zinc α -hydroxyglutarate.

† At 16°.

‡ From the silver salt.

§ In dil. NaOH (3 mol.).

principal lines; for others, and for the curves, the original should be consulted.

J. C. W.

Bile Acids. V. The Reduction of Dehydrocholic and Dehydrodeoxycholic Acids. HEINRICH WIELAND and ERICH BOERSCH (*Zeitsch. physiol. Chem.*, 1919, **106**, 190—201).—*Dehydroisodeoxycholic acid* (β -diketocholanic acid), $C_{24}H_{38}O_4$, was prepared as its ethyl ester by reducing an alcoholic solution of dehydrocholic acid with granulated zinc and hydrochloric acid in presence of mercuric chloride; it crystallises in colourless needles, m. p. 177° ; the ethyl ester forms lustrous needles, m. p. 152.5° .

Cholanic acid, $C_{24}H_{40}O_2$, is obtained from dehydrocholic acid by boiling with zinc amalgam and concentrated hydrochloric acid for twelve hours, and then passing hydrogen chloride into the boiling solution for ten hours. The ethyl ester crystallises in shining fragments, m. p. $93-94^\circ$, $[\alpha]_D^{25} + 20.97^\circ$. The acid forms voluminous clusters of needles, m. p. $163-164^\circ$, $[\alpha]_D^{25} + 21.74^\circ$ in chloroform solution.

α -Ketocholanic acid, $C_{24}H_{38}O_3$, is obtained as the ethyl ester, by reducing an alcoholic solution of dehydrodeoxycholic acid with zinc amalgam and concentrated hydrochloric acid. The ethyl ester forms colourless needles, m. p. 95° ; the acid crystallises in broad, colourless leaves, m. p. 183° .

Hydroxyketocholanic acid, $C_{24}H_{38}O_4$, also obtainable by reduction of dehydrodeoxycholic acid, forms soft, lustrous needles, m. p. 161° ; the ethyl ester forms lustrous prisms, m. p. 133° .

S. S. Z.

The Oxidation of Organic Compounds with Alkaline Potassium Permanganate. I. The Oxidation of Acetaldehyde. II. The Oxidation of Ethylene Glycol, Glycolaldehyde, Glyoxal, Glycollic Acid, and Glyoxylic Acid.

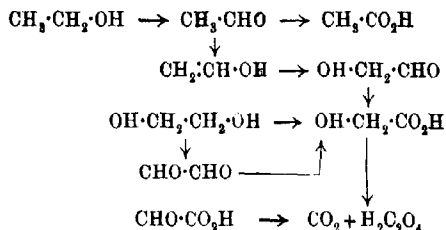
WILLIAM LLOYD EVANS and HOMER ADKINS (*J. Amer. Chem. Soc.*, 1919, **41**, 1385—1414. Compare this vol., i, 514).—I. A solution of potassium permanganate, containing 15 grams per litre and various proportions of potassium hydroxide, was reduced by a 2-molar solution of acetaldehyde at 25° , 50° , and 75° , the quantity of aldehyde being recorded, and also the weights of the various oxidation products. The results are tabulated and reproduced by curves. Within certain limits, the quantity of acetic acid produced is a function of the concentration of potassium hydroxide. When plotted on logarithmic paper, the concentrations fall on a straight line, from which the equation $\log Y = \log B - a \log X$ may be deduced, where Y = the number of grams of acetic acid produced by the oxidation of 0.1 gram-mol. of acetaldehyde at a concentration of X grams of potassium hydroxide per litre and a = the tangent of the angle which the line makes with the X axis. The limits are as follows: at 25° , 1.95 to 90 grams; at 50° , 1.3 to 32.5 grams; at 75° , 0.85 to 18.5 grams. Below the smaller values, the

oxidation to acetic acid is quantitative; above the higher values, the concentration of alkali has no influence on the yield of acetic acid. Within these limits, the yield of acetic acid decreases with increasing alkalinity and rise of temperature. The other oxidation products are oxalic acid and carbon dioxide. These increase with rise of temperature and alkalinity, but again there are limits above which the concentration of alkali is immaterial. The most instructive reproduction of the yields of these products is given in curves connecting the alkali concentrations with the weights of oxalic acid or carbon dioxide which would be produced if 0.1 molar quantities of acetaldehyde or an intermediate compound were oxidised to oxalic acid and carbon dioxide in the ratio in which they are produced in the particular experiment. For example, if in a given experiment 1 gram of oxalic acid and 1 gram of carbon dioxide were produced, the acetaldehyde equivalent would be 0.49 and 0.50 gram respectively. Then, if a total of 0.99 gram of acetaldehyde produces 1 gram of oxalic acid, 4.4 grams (0.1 mol.) would yield 4.44 grams. The ratio of oxalic acid to carbon dioxide rises with increase of temperature and alkalinity, but the curves connecting alkali concentrations with the above quantities are straight lines if plotted on logarithmic paper. That is, the weight of substance converted into oxalic acid or carbon dioxide compared with the total amount converted into oxalic acid plus carbon dioxide is a simple function of the alkali concentration. In other words, the alkali acts in the same general way on the precursor of these products as it does on the acetaldehyde from which the acetic acid is formed.

II. The oxidation of ethylene glycol, glycollaldehyde, glyoxal, glycollic acid, and glyoxylic acid was studied at 50° in the same manner. Ethylene glycol yields carbon dioxide and oxalic acid; with less than 0.5 gram of potassium hydroxide per litre, the sole product appears to be carbon dioxide, then up to 3 grams per litre the yield of carbon dioxide falls and that of oxalic acid rises uniformly, after which the concentration of alkali has no influence on the ratio between the two products. Glycollaldehyde also produces carbon dioxide in falling amounts and oxalic acid in increasing quantities, but the yields are logarithmic functions of the alkali concentration. Glyoxal behaves more like ethylene glycol; the yields are linear functions of the alkali concentrations up to 45.5 grams potassium hydroxide per litre, when further alkali is without effect on the yields, that of oxalic acid being 76.7%. Glycollic acid yields the same proportions of oxalic acid and carbon dioxide regardless of whether the initial concentration of potassium hydroxide is 0.68 or 48 grams per litre. Glyoxylic acid corresponds with glycollaldehyde; the yields are logarithmic functions of the alkali concentrations.

The curves connecting the yields of oxalic acid and carbon dioxide at 50° with alkali concentrations are absolutely identical in the cases of acetaldehyde and glycollaldehyde. It is therefore highly probable that glycollaldehyde is an intermediate product in the oxidation of acetaldehyde by alkaline permanganate, and the

whole scheme for the oxidation of these compounds with two carbon atoms may be written thus:



J. C. W.

The Stabilisation of Acraldehyde. I. The Methods of Spontaneous Alteration of Acraldehyde. CHARLES MOUREU and CHARLES DUFRAISSE (*Compt. rend.*, 1919, **169**, 621—626).—Acraldehyde, when kept, undergoes spontaneous change in one of two directions, giving either an insoluble resin, disacryl, or a soluble resin. The velocity of change into the insoluble resin is accelerated by the presence of impurities, by rise in temperature, or by an increase in the intensity of illumination. The cause of the fracture of glass vessels in which this change occurs is shown to be purely physical.

The second change into a soluble resin is accelerated by the presence of a free base, metallic salts, or certain compounds, such as hydrogen sulphide, the chlorides of arsenic, antimony, bismuth, or tin, and nitrogenous organic substances. Rise in temperature also accelerates the change.

These two different methods of spontaneous alteration of acraldehyde cannot, apparently, proceed simultaneously in the same sample, although in some cases one change may proceed for a time and then be replaced by the other.

W. G.

The Stabilisation of Acraldehyde. II. Empirical Process of Stabilisation. CHARLES MOUREU and ADOLPHE LÉPAGE (*Compt. rend.*, 1919, **169**, 705—708. Compare Moureu and Dufraisse, preceding abstract).—The process of stabilisation recommended is to shake the crude acraldehyde, prepared by the dehydration of glycerol, with 10% of its weight of dry sodium hydrogen carbonate. The product thus obtained is stable for a long time if it is kept in the absence of air, not exposed to sunlight, and at a temperature not exceeding 30°. The crude acraldehyde contains certain impurities which tend to prevent its conversion into insoluble resin, whilst other impurities accelerate its conversion into soluble resin.

W. G.

Preparation of Anhydrous Dextrose Sodium Iodide. JOHANN A. WÜLFING (D.R.-P. 312643; from *Chem. Zentr.*, 1919, iv, 147).—Anhydrous dextrose and anhydrous sodium iodide, in

the proportion of at least two molecules of the former to one molecule of the latter, are mixed as intimately as possible, and the mixture is melted or moistened with strong alcohol and dried at 100–115°. In either case, the proportion of two molecules of dextrose may be exceeded, whereby the mass becomes more easily melted or pulverised. The double compound, $(C_6H_{12}O_6)_2 \cdot NaI$, exists in the anhydrous and hydrated states ($+ H_2O$). In the former condition it is not hygroscopic, whilst in the latter state it is as hygroscopic as sodium iodide. The yield of the anhydrous substance is quantitative, whilst that obtained in accordance with D.R.-P. 196605 (A., 1908, i, 765) is considerably smaller.

H. W.

Solubility of Lactose. Action of Acids and Alkalis on Lactose. E. SAILLARD (*Chim. et Ind.*, 1919, 2, 1035–1036).—The solubility of lactose at various temperatures was found to be as follows, the solubility of sucrose under the same conditions below given for comparison:

Temperature.	Kilo. of sugar per 1 kilo. of water.	
	Anhydrous Lactose.	Sucrose.
21.5°	0.20	2.06
28.0	0.24	2.16
38.0	0.307	2.34
48.0	0.421	2.55
57.0	0.56	2.78
65.0	0.77	3.03

Lactose is hydrolysed completely in ninety minutes when heated at 90° with 10% hydrochloric acid, but is not appreciably attacked by 10% acetic acid. When lactose is heated at 90° with 1% sodium hydroxide solution, about 64% of the alkali is neutralised and 85% of the sugar destroyed within two hours.

W. P. S.

Predominating Influence of the Degree of Dispersion of Starch Solutions on the so-called Starch Coagulation.

HERMANN SALLINGER (*Kolloid Zeitsch.*, 1919, 25, 79–81).—The coagulation of solutions of soluble starch by means of ptyalin (from human saliva) has been investigated. It is shown that the coagulation takes place sooner the larger the quantity of ptyalin added, and that the amount of coagulated starch decreases, whilst the quantity of maltose formed increases with the amount of ptyalin added. A similar starch solution heated to 110° under a pressure of 1.5 atms. before treatment was coagulated much more slowly, gave about a quarter as much coagulum, but rather more maltose, than the unheated starch. The experiments show the influence of the dispersity on the coagulation, and they also confirm the view of Lintner that it is unnecessary to assume the presence of an enzyme amylcoagulase in malt extract which is capable of affecting the coagulation of starch. The coagulation is brought about by the conversion of the protecting colloid, the starch sol, into sugar, which thereby causes the starch gel to coagulate.

J. F. S.

Synthesis of Polypeptides of which Cystine forms a Constituent. E. ABDERHALDEN and HANS SPINNER (*Zeitsch. physiol. Chem.*, 1919, **106**, 296—309).—The following polypeptides have been synthesised:

Dichloroacetyl-L-cystine crystallises from ethyl acetate in clusters of fan-shaped prisms, m. p. 137—139°, or from water in silky spheres of long needles with one molecule of water, m. p. 96—98°. It shows weak mutarotation.

Diglycyl-L-cystine, a white, amorphous powder, decomposes at 200°, and has $[\alpha]_D^{25} = -111.4^\circ$ to -116.54° in aqueous solution.

Di- α -bromo-D-isohexoyldiglycyl-L-cystine is a yellowish-white powder, and in alcoholic solution has $[\alpha]_D^{25} = -8.37^\circ$ to -18.2° .

Di-L-leucyldiglycyl-L-cystine turns brown at 220°, and in aqueous solution has $[\alpha]_D^{25} = -78.6^\circ$ to -80.99° .

Dichloroacetyldi-L-leucyldiglycyl-L-cystine is a light yellow powder, and in alcoholic solution has $[\alpha]_D^{25} = -32.8^\circ$ to -42.85° .

Diglycyl-di-L-leucyldiglycyl-L-cystine, a light yellow powder, has in aqueous solution $[\alpha]_D^{25} = -81.78^\circ$.

Dibromo-D-isohexoyldiglycyl-di-L-leucyldiglycyl-L-cystine forms a yellow powder.

The action of alcoholic-aqueous ammonia and of alcoholic ammonia on dichloroacetyl-L-cystine is described. S. S. Z.

Bile Acids. IV. The Synthesis of Glycodeoxycholic and Taurodeoxycholic Acids. HEINRICH WIELAND [with FR. LUDWIG STENDER] (*Zeitsch. physiol. Chem.*, 1919, **106**, 181—190. Compare A., 1916, i, 710).—*Deoxycholic acid hydrazide*, $C_{24}H_{42}O_3N_2$, prepared from the acid deoxycholic ester and hydrazine hydrate, forms colourless needles, m. p. 208°. The hydrazide was then converted into the amorphous *acid* by treating it with hydrochloric acid and sodium nitrite. From the azide, *glycodeoxycholic acid* was synthesised by a modification of the method which Bondi and Müller used in the preparation of glycocholic acid; it forms colourless needles, m. p. 187—188° (decomp.), and contains one molecule of water, which is lost on heating at 150° in a vacuum.

Taurodeoxycholic acid, $C_{26}H_{44}O_5 \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot SO_3H$, was prepared from deoxycholic acid azide in the form of colourless, hygroscopic, prismatic needles grouped in rosettes, m. p. 175—200°, not sharp.

Attempts to prepare glycocholeic and taurocholeic acids by combining the conjugated deoxycholic acids with stearic acid failed. The nature and origin of the glycocholeic and taurocholeic acids prepared from the bile are discussed. S. S. Z.

Crystallography of some Platinithiocyanates of Organic Bases. E. QUERCIGH (*Riv. Min. Crist. Ital.*, 1915, **44**, 17—25).—The guanidine salt is trigonal, the piperidine salt hexagonal-pyramidal, and the diacetoneamine salt monoclinic. Complete crystallographic data are given. CHEMICAL ABSTRACTS.

Oxidation Potential of Ferri-Ferrocyanide Solution. I. M.

KOLTHOFF (*Chem. Weekblad*, 1919, 16, 1406—1415).—The influence of the hydrogen ions on the oxidation potential of solutions of potassium ferri-ferrocyanide has been investigated by the author. A considerable increase of potential was obtained by the addition of even 0.012*N*-hydrogen chloride, and, taking the average for various determinations with different concentrations of hydrochloric acid, it was found that $\epsilon = 0.416 - 0.0577 \log (\text{HCl})^{3.22}$. The influence of the acid is explained by the fact that the third and fourth dissociation constants of hydroferrocyanic acid are comparatively small, whilst hydroferrieyanic acid is a strong acid. The concentration of the ferrocyanide ions thus becomes much lower on acidifying. The fourth dissociation constant of hydroferrocyanic acid is about 5×10^{-4} .

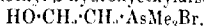
The author found no difference in the physical properties (except the colour) of solutions of α - and β -potassium ferrocyanide.

References to the results of other investigators are given.

W. J. W.

Ethanoltrialkylarsonium Hydroxides. M. GUGGENHEIM and

E. HUG (U.S. Pat. 1308413).—Trimethyl- β -bromoethylarsonium bromide, prisms, m. p. 239°, is prepared by heating 5 parts of trimethylarsine and 7.5 parts of ethylene dibromide for three hours at about 100°. Three parts of this product may be hydrolysed by heating with 10 parts of water at 180° for four hours. Ethanoltrimethylarsonium [trimethyl- β -hydroxyethylarsonium] bromide,



thus formed, is converted into the free base by the action of silver oxide. β -Bromotetraethylarsonium bromide, prismatic crystals, m. p. 225°, may be obtained similarly from triethylarsine. The product may be hydrolysed to form β -hydroxytetraethylarsonium bromide, and the latter can be converted into the free base by the action of silver oxide. Trimethyl- β -hydroxyethylarsonium hydroxide is a syrup which partly crystallises and has an odour like that of trimethylarsine. It is readily soluble in water or alcohol, and forms a crystalline chloride, m. p. 230°, which is soluble in alcohol.

CHEMICAL ABSTRACTS.

Ethanoltrialkylarsonium Compounds. M. GUGGENHEIM and

E. HUG (U.S. Pat. 1308414). Eighteen parts of trimethylarsine and 20 parts of ethylene chlorohydrin are heated together at 120–125° for four hours. The product, which is partly solidified, is dissolved in alcohol, and, after concentration of the solution, ether is added to precipitate ethanoltrimethylarsonium [trimethyl- β -hydroxyethylarsonium] chloride, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{AsMe}_3\text{Cl}$, which may be converted into the hydroxide by the action of silver oxide. Ethylene bromohydrin may be used instead of the chlorohydrin in effecting the reaction. Triethylarsine, when used as starting material, yields similar products, containing ethyl instead of

methyl. The ethanoltriakylarsonium hydroxides and their salts are stated to possess valuable therapeutic properties.

CHEMICAL ABSTRACTS.

Relations between the Constitution and the Physical Properties of the Hydrocarbons of the Benzene Series.

K. VON AUWERS (*Annalen*, 1919, **419**, 92—120. Compare A., 1916, i, 130).—Examination of the physical constants of twenty-four hydrocarbons has shown that the compounds with ortho-side-chains occupy a peculiar position; whilst the density and refractive index are higher than those of their isomerides, the exaltations of refractive and dispersive power are lower. In general, the boiling points of ortho-derivatives are higher than those of the isomeric hydrocarbons, although the differences are frequently small. The differences between the constants of ortho- and vicinal derivatives and those of their isomerides are much greater than the small discrepancies observed between different specimens of the same substance as far as carefully purified material and accurate observation are concerned. The influences of constitution on the refractive and dispersive powers of position isomeric aromatic hydrocarbons can only be detected with certainty in the cases of substances with neighbouring side-chains; the differences caused in the meta- and para-series lie within the limits of experimental error.

The methods chiefly used in the preparation of the hydrocarbons are the Fittig synthesis, the elimination of amino-groups from the corresponding amines by Friedländer's method, and the reduction of suitable ketones with amalgamated zinc and hydrochloric acid according to Clemmensen. The following constants are recorded.

Benzene has b. p. 80° , D_4^{15} 0.8867, D_4^{20} 0.880, n_D^{15} 1.50119, $n_D^{12.5}$ 1.50565, $n_D^{12.5}$ 1.51817, $n_D^{12.5}$ 1.52867, n_D^{20} 1.5022. Toluene has b. p. $109-110^{\circ}$, D_4^{15} 0.8684, D_4^{20} 0.866, n_D^{15} 1.49365, $n_D^{15.5}$ 1.49782, $n_D^{16.5}$ 1.50967, $n_D^{16.5}$ 1.51970, n_D^{20} 1.4962. Ethylbenzene has b. p. $135-136^{\circ}$, D_4^{15} 0.8708, D_4^{20} 0.866, $n_D^{15.5}$ 1.49423, $n_D^{15.5}$ 1.49828, $n_D^{15.5}$ 1.50953, $n_D^{15.5}$ 1.51904, n_D^{20} 1.4960. Propylbenzene has b. p. $158-159^{\circ}$, D_4^{15} 0.8681, D_4^{20} 0.862, $n_D^{15.5}$ 1.49176, $n_D^{15.5}$ 1.49549, $n_D^{15.5}$ 1.50630, $n_D^{15.5}$ 1.51533, n_D^{20} 1.4920. *iso*Propylbenzene has b. p. $152.8-153.4^{\circ}$, D_4^{15} 0.8662, D_4^{20} 0.864, $n_D^{15.5}$ 1.49063, $n_D^{15.5}$ 1.49441, $n_D^{15.5}$ 1.50539, $n_D^{15.5}$ 1.51466, n_D^{20} 1.4930.

For *o*-xylene the following data are given: I. Commercial specimen rectified over sodium, b. p. $142-142.5^{\circ}$, D_4^{15} 0.8798, D_4^{20} 0.878, $n_D^{15.5}$ 1.50090, $n_D^{15.5}$ 1.50491, $n_D^{15.5}$ 1.51668, $n_D^{15.5}$ 1.52659, n_D^{20} 1.5040. II. Specimen from *o*-iodotoluene, methyl iodide, and sodium in warm ethereal solution: b. p. 142° , D_4^{15} 0.8825, D_4^{20} 0.879, $n_D^{15.5}$ 1.50248, $n_D^{15.5}$ 1.50664, $n_D^{15.5}$ 1.51846, $n_D^{15.5}$ 1.52838, n_D^{20} 1.5049. III. Specimen from pure *o*-3-xylidine through the diazo-compound: b. p. $142-143^{\circ}$, D_4^{15} 0.8837, D_4^{20} 0.880, $n_D^{15.5}$ 1.50368, $n_D^{15.5}$ 1.50777, $n_D^{15.5}$ 1.51960, $n_D^{15.5}$ 1.52958, n_D^{20} 1.5057. *m*-Xylene, prepared from *m*-xylylic acid, has b. p. $135-136^{\circ}$, D_4^{15} 0.8666, D_4^{15} 0.8667, D_4^{20} 0.864, $n_D^{15.5}$ 1.49429, $n_D^{15.5}$ 1.49830, $n_D^{15.5}$ 1.51007, $n_D^{15.5}$ 1.51997, n_D^{20} 1.4970, whilst when prepared from *m*-xylidine it has b. p. 137.5° , D_4^{15} 0.8686,

D_1^{20} 0.865, $n_D^{14.5}$ 1.49548, $n_D^{14.5}$ 1.49962, $n_D^{14.5}$ 1.51128, $n_D^{14.5}$ 1.52112, n_D^{20} 1.4973. For *p*-xylene the following constants are recorded: I. Museum specimen, b. p. 135—136°, $D_4^{17.2}$ 0.8627, $D_4^{17.5}$ 0.8625, D_4^{20} 0.861, $n_D^{17.5}$ 1.49273, $n_D^{17.5}$ 1.49682, $n_D^{17.5}$ 1.50849, $n_D^{17.5}$ 1.51841, n_D^{20} 1.4957. II. Kahibaum's product distilled over sodium, b. p. 136—137°, $D_4^{16.1}$ 0.8659, $D_4^{16.2}$ 0.8658, D_4^{20} 0.863, $n_D^{16.2}$ 1.49357, $n_D^{16.2}$ 1.49760, $n_D^{16.2}$ 1.50925, $n_D^{16.2}$ 1.51907, n_D^{20} 1.4959. III. Specimen from *p*-dibromobenzene, b. p. 135—136°, $D_4^{16.2}$ 0.8624, D_4^{20} 0.859, $n_D^{16.2}$ 1.49335, $n_D^{16.2}$ 1.49734, $n_D^{16.2}$ 1.50912, $n_D^{16.2}$ 1.51902, n_D^{20} 1.4956.

o-Methylethylbenzene has b. p. 164.8—165°, $D_4^{15.7}$ 0.8841, D_4^{20} 0.881, $n_D^{15.7}$ 1.50213, $n_D^{15.7}$ 1.50611, $n_D^{15.7}$ 1.51745, $n_D^{15.7}$ 1.52693, n_D^{20} 1.5042.

m-Methylethylbenzene has b. p. 161.5—162.5°, $D_4^{17.8}$ 0.8690, D_4^{20} 0.867, $n_D^{17.9}$ 1.49456, $n_D^{17.9}$ 1.49849, $n_D^{17.9}$ 1.50973, $n_D^{17.9}$ 1.51920, n_D^{20} 1.4975.

p-Methylethylbenzene (from *p*-bromotoluene) has b. p. 161—162°, D_4^{20} 0.8601, D_4^{20} 0.8597, D_4^{20} 0.862, $n_D^{22.8}$ 1.48921, $n_D^{22.8}$ 1.49303, $n_D^{22.8}$ 1.50417, $n_D^{22.8}$ 1.51353, n_D^{20} 1.4943, whilst when prepared from *p*-tolyl methyl ketone it has b. p. 161—162°, $D_4^{17.1}$ 0.8687, ($D_4^{17.4}$ 0.8685), D_4^{20} 0.863, $n_D^{17.4}$ 1.49588, $n_D^{17.4}$ 1.50004, $n_D^{17.4}$ 1.51130, $n_D^{17.4}$ 1.52116, n_D^{20} 1.4971.

o-Methylpropylbenzene has b. p. 184°, $D_4^{15.75}$ 0.8770, D_4^{20} 0.874, $n_D^{15.75}$ 1.49765, $n_D^{15.75}$ 1.50139, $n_D^{15.75}$ 1.51218, $n_D^{15.75}$ 1.52125, n_D^{20} 1.4995.

m-Methylpropylbenzene has b. p. 181.5—182.5°, $D_4^{17.8}$ 0.8690, D_4^{20} 0.8648, D_4^{20} 0.862, $n_D^{17.9}$ 1.49262, $n_D^{17.9}$ 1.49640, $n_D^{17.9}$ 1.50738, $n_D^{17.9}$ 1.51646, n_D^{20} 1.4951.

p-Methylpropylbenzene has b. p. 182—183°, $D_4^{15.4}$ 0.8642, D_4^{20} 0.861, $n_D^{15.4}$ 1.49371, $n_D^{15.4}$ 1.49749, $n_D^{15.4}$ 1.50863, $n_D^{15.4}$ 1.51804, n_D^{20} 1.4954.

o-Methylisopropylbenzene (*o*-cymene) has b. p. 175—176°, $D_4^{16.15}$ 0.8789, D_4^{20} 0.876, $n_D^{16.15}$ 1.49826, $n_D^{16.15}$ 1.50206, $n_D^{16.15}$ 1.51290, $n_D^{16.15}$ 1.52185, n_D^{20} 1.5003.

m-Methylisopropylbenzene has b. p. 175°, $D_4^{17.05}$ 0.8628, D_4^{20} 0.860, $n_D^{17.05}$ 1.49016, $n_D^{17.05}$ 1.49385, $n_D^{17.05}$ 1.50452, $n_D^{17.05}$ 1.51336, n_D^{20} 1.4925.

p-Methylisopropylbenzene, from toluene, isopropyl bromide, and aluminium chloride, has b. p. 175—176°, $D_4^{15.0}$ 0.8631, D_4^{20} 0.859, $n_D^{15.0}$ 1.49105, $n_D^{15.0}$ 1.49474, $n_D^{15.0}$ 1.50537, $n_D^{15.0}$ 1.51449, n_D^{20} 1.4925; the physical constants are also recorded for specimens obtained commercially, from camphor and phosphoric oxide, from α -terpineol by Wallach's method, and from 1-methyl-4- $\beta\beta$ -dichloroisopropylbenzene by reduction with sodium and alcohol.

p-Diethylbenzene has b. p. 183°, $D_4^{16.2}$ 0.8678 ($D_4^{16.2}$ 0.8679), D_4^{20} 0.865, $n_D^{16.2}$ 1.49499, $n_D^{16.2}$ 1.49897, $n_D^{16.2}$ 1.50993, $n_D^{16.2}$ 1.51924, n_D^{20} 1.4973.

Hemimellitene has b. p. 175—176°, 744 mm., $D_4^{15.35}$ 0.8949, D_4^{20} 0.895, $n_D^{15.35}$ 1.50930, $n_D^{15.35}$ 1.51335, $n_D^{15.35}$ 1.52503, $n_D^{15.35}$ 1.53483, n_D^{20} 1.5132.

ψ -Cumene has b. p. 168.7—169.2°, $D_4^{15.0}$ 0.8794, D_4^{20} 0.876, $n_D^{15.0}$ 1.50259, $n_D^{15.0}$ 1.50672, $n_D^{15.0}$ 1.51841, $n_D^{15.0}$ 1.52816, n_D^{20} 1.5046.

Mesitylene has b. p. 165—166°, $D_4^{17.05}$ 0.8646, D_4^{20} 0.862, $n_D^{17.05}$ 1.49403, $n_D^{17.05}$ 1.49804, $n_D^{17.05}$ 1.50936, $n_D^{17.05}$ 1.51891, n_D^{20} 1.4967.

1:2:3:4-Tetramethylbenzene has b. p. 203—204°, D_4^{16} 0.9044, D_4^{20} 0.901, n_D^{16} 1.51621, n_D^{16} 1.52031, n_D^{16} 1.53192, n_D^{16} 1.54189, n_D^{20} 1.5185.

1:2:5-Trimethyl-4-ethylbenzene has b. p. 211°, $D_4^{15.85}$ 0.8866, ($D_4^{15.75}$ 0.8867), D_4^{20} 0.883, $n_D^{15.75}$ 1.50654, $n_D^{15.75}$ 1.51047, $n_D^{15.75}$ 1.52163, $n_D^{15.75}$ 1.53112, n_D^{20} 1.5086.

1:3:5-Trimethyl-2-ethylbenzene has b. p. 210.2°/753 mm., $D_4^{16.25}$ 0.8885, D_4^{20} 0.886, $n_D^{16.25}$ 1.50875, $n_D^{16.25}$ 1.51274, $n_D^{16.25}$ 1.52416, $n_D^{16.25}$ 1.53376, n_D^{20} 1.5111.

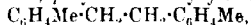
H. W.

Pyro-condensations in the Aromatic Series. HANS MEYER and ALICE HOFMANN (*Monatsh.*, 1916, **37**, 681—722).—The first of three papers on this subject, the second having already been reviewed in A., 1917, i, 641, and the third in A., 1918, i, 66. The object of the initial investigation was to study the products formed by the decomposition of the vapours of non-halogenated aromatic compounds at the lowest possible temperatures, the method being similar to that described in a series of papers by Löb (1901—1905).

Benzene begins to decompose into diphenyl at 650° (compare Smith and Lewcock, T., 1912, **101**, 1453).

When kept for a few hours at a dull red heat, toluene vapour gives almost exclusively dibenzyl, the product which is formed when toluene is oxidised with potassium persulphate in the cold (Moritz and Wollenstein, A., 1899, i, 424). At a bright red heat, however, hydrogen is also lost from the nucleus. The hydrocarbons which may be frozen out from the mixture at -80° include dibenzyl, stilbene, and anthracene (see below), whilst a study of the oxidation products of the remaining oil reveals the probable presence of di-*p*-tolyl and *p*-methyldiphenylmethane.

At a bright red heat, *p*-xylene readily yields *p*-dixylyl,

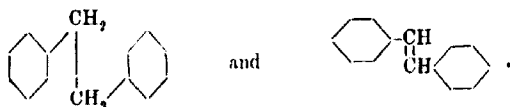


m. p. 81—82° (*ibid.*), but at a higher temperature (yellow heat) more oil is produced. The chief by-product is *pp'*-dimethylstilbene.

Mesitylene decomposes very smoothly, giving dimesityl.

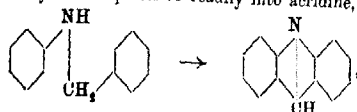
Ethylbenzene gives chiefly stilbene and an oily by-product, which only yields benzoic acid on oxidation, and therefore contains no hydrocarbons with condensed nuclei. The production of stilbene may be due to the elimination of methane and the union of the :CHPh residues, or to condensation to $\beta\gamma$ -diphenylbutane and loss of ethylene.

Dibenzyl gives stilbene and a very little toluene, with considerable quantities of anthracene, but no trace of phenanthrene. Stilbene, however, gives no anthracene or phenanthrene. This remarkable difference between dibenzyl and stilbene is explained by assuming that the positive methylene groups in the former bring the negative benzene nuclei close to the connecting chain, whereas the negative ethylene linking in stilbene keeps the nuclei at a distance, thus:

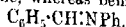


Several facts support this idea. In the first place, dihydroanthracene, which should be the primary product from dibenzyl, passes rapidly into anthracene at a red heat, and *p*-xylene or *p*-dixylyl gives 2:6-dimethylantracene at a bright red heat,

whereas mesitylene or dimesityl forms no anthracene derivative. Similarly, benzyaniline passes so readily into acridine,



that this pyrogenic method may be employed with advantage in the preparation of acridine, whereas benzyldeneaniline,



only yields aniline, benzonitrile, benzene, diphenyl, and such products.

Benzanilide gives a good yield of phenanthridone, *m. p.* 290°, which is reduced to phenanthridine by distillation over zinc dust.

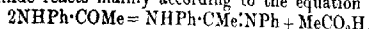
When diphenylmethane vapour is exposed to the glowing platinum spiral for seven hours, the products are benzene, toluene, a trace of diphenyl, and small quantities of anthracene, but chiefly fluorene, the process ranking as a convenient synthesis of this hydrocarbon. It is stated that Carnelley's "γ-methylenediphenyl" is only fluorene, and his "δ-methylenediphenyl" is most probably anthracene (*T.*, 1880, **37**, 708).

Benzophenone is not easily changed, but the initial products are benzene and benzaldehyde.

Diphenyl ether readily yields diphenylene oxide, *m. p.* 81°.

Diphenylamine gives carbazole and some hydrogen cyanide, but di-*a*-naphthylamine loses ammonia and forms naphthalene instead of a substituted carbazole.

Acetanilide reacts mainly according to the equation



The bases are extracted from the ethereal solution of the product and then submitted to distillation in steam, when small quantities of aniline and *o*-aminoacetophenone (recognised by its jasmine-like odour) pass over, leaving a little *p*-aminoacetophenone and the diphenylethenylamidine behind.

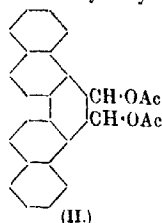
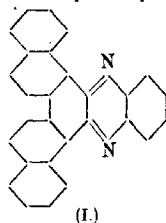
Naphthalene decomposes into ββ-dinaphthyl at a dull red heat, but as the temperature is raised more and more αα-dinaphthyl is formed. The so-called αβ-dinaphthyl (Smith, *T.*, 1877, **32**, 559; Wegscheider, *A.*, 1891, 216) is probably impure αα-dinaphthyl.

Diphenyl gives 4:4'-diphenyldiphenyl, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5$, *m. p.* 310°. *o-o'*-Ditolyl, from *o*-iodotoluene by heating with copper at 250°, reacts rapidly at the glowing spiral to form phenanthrene, which apparently gives diphenanthryl when the heating is continued. Anthracene gives 5:5'-dianthryl, but anthraquinone residues link up in the 2:2'-positions.

Weger reported the production of naphthalene by the passage of cyclopentadiene vapours through a red-hot tube (*Zeitsch. angew. Chem.*, 1909, **22**, 344), but this must have been due to the total disruption of the molecule and rebuilding from the ethylene and acetylene produced. Under the present conditions, no naphthalene

could be found, the products being partly evil-smelling oils and partly soluble or insoluble, but amorphous, solids.

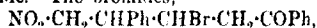
The so-called "Crackene" [with PAUL R. VON LENDENFELD].—Klaudy and Fink (A., 1900, i, 284) isolated "crackene" from the so-called red pitch formed in the "cracking" of oils, and suggested that it might be identical with "benzerythrene," since proved to be the above 4:4'-diphenyldiphenyl, but certainly not with picene. The present authors were struck with the fact that various fractions of the hydrocarbon varied slightly in colour. By treatment with a small quantity of bromine in warm chloroform, followed by repeated crystallisations from boiling xylene, they have succeeded in removing a coloured impurity and establishing the substance as picene. Picene may be characterised by conversion into picenequinone, and formation from this of *picenequinoruline* (I), microscopic, yellow needles, by condensation with *o*-phenylenediamine. Picenequinone also forms a yellowish-brown *diacetyl* derivative (II), which may be hydrolysed to a dark dihydroxy-derivative.



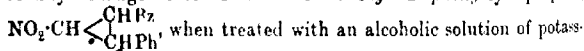
The acetylation is therefore accompanied by reduction. Picene and benzerythrene are said to dissolve in concentrated sulphuric acid with green colour. The pure hydrocarbons really give colourless solutions, picene exhibiting pale blue fluorescence.

J. C. W.

The cycloPropane Series. VII. Nitrocyclopropanes. E. P. KOHLER and H. F. ENGELBRECHT (*J. Amer. Chem. Soc.*, 1919, 41, 1379—1384. Compare this vol., i, 533).—Phenyl styryl ketone condenses with nitromethane to form phenyl γ -nitro- β -phenylpropyl ketone, which yields two α -bromo-derivatives when treated with bromine in chloroform. The principal product has m. p. 100°, and is transformed into the isomeride, m. p. 106° (not 86°, as given in A., 1916, i, 404), by crystallising from an alcoholic solution of hydrogen bromide. The bromides,



readily change into 3-nitro-1-benzoyl-2-phenylcyclopropane,



ium acetate. The compound crystallises in clusters of stout prisms, m. p. 98°, and is changed by the action of hydrogen bromide dissolved in acetic acid into phenyl γ -bromo- β -nitro- γ -phenylpropyl ketone, $\text{CHPhBr}\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{COPh}$, which forms colourless plates, m. p. 115–116°, and becomes yellow in sunlight. This

ketone is very sensitive. When boiled with methyl alcohol and a little ammonium bromide, for example, it changes into 2:5-diphenyl-furan, and when heated above its m. p. it gives a pale yellow substance, plates, m. p. 77° , which is probably 3-bromo-1:5-diphenyl-furan. The cyclopropane derivative reacts most readily with bases, but the products are complex mixtures. With sodium methoxide solution, under special conditions, it is possible to isolate $\alpha\delta$ -diphenylbutan- $\alpha\gamma$ -dione, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COPh}$. J. C. W.

Decomposition of Tetranitromethylaniline [2:4:6-Trinitrophenylmethylnitroamine]. EDMUND VON HERZ (*Z. ges. Schiess. u. Sprengstoffw.*, 1919, **14**, 155--157; from *Chem. Zentr.*, 1919, iv, 163).—The author's previous conclusion that the decomposition can be caused by electrolytic processes is confirmed by further laboratory experiments. Diazo-compounds similar to dinitrobenzoquinonediazide are probably formed, and not azide substances, such as $\text{O}:\text{C}_6\text{H}_2(\text{NO}_2)_2 < \begin{smallmatrix} \text{N} \\ \diagup \diagdown \end{smallmatrix}$. It is certain that the reac-

tions which result in the decomposition products affect the benzene nucleus exclusively; the occurrence of ammonia, methylamine, etc., is due solely to secondary changes, and has no influence on the characteristic transformation of the nucleus. The observed phenomena are not a specific property of tetryl, but are common to all trinitro-derivatives of benzene, such as trinitro-benzene, -toluene, -phenol, and -cresol. Decompositions of mercury fulminate in zinc capsules covered with an inner cap of copper or brass are probably also to be attributed to local electric currents. H. W.

Proteinogenous Amines. V. The Preparation of *p*-Hydroxyphenylethylamine Hydrochloride (Tyramine Hydrochloride). KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, **39**, 585--592).—Certain improvements in the method for the synthesis of *p*-hydroxyphenylacetone-nitrile as given by Pschorr, Wolfes, and Buckow (*A.*, 1900, i, 170) are recorded. The reduction of this substance is effected by a method which it is claimed is more satisfactory than that employed by Barger (*T.*, 1909, **95**, 1127). The *p*-hydroxyphenylacetone-nitrile is dissolved in alcohol and treated with sodium, and after reduction is completed, the solution is rendered acid with hydrochloric acid. *p*-Cresol and *p*-hydroxyphenylacetic acid may then be removed by extraction with ether, after which the solution is rendered strongly alkaline and the tyramine is extracted with amyl alcohol. The amine may be extracted from the amyl alcohol by shaking with dilute hydrochloric acid. Yield, 58% of theoretical. The *p*-cresol and *p*-hydroxyphenylacetic acid present in the ethereal extract may be separated and isolated by shaking with sodium carbonate solution. The ethereal fraction retains the *p*-cresol, whilst the alkaline aqueous solution removes the *p*-hydroxyphenylacetic acid. J. C. D.

The Problem of the Physiological Polypeptide Synthesis. EMIL ABDERHALDEN and HANS SPINNER (*Zeitsch. physiol. Chem.*, 1919, **106**, 309--312).—By treating glycine with benzaldehyde in

absolute alcohol and sodium hydroxide, a condensation product identical with the benzylidene compound of *isodiphenyloxethylamine* is obtained in small needles, m. p. 132°. By treating glycine dissolved in sodium hydroxide with benzaldehyde and then oxidising with potassium permanganate, benzoic and hippuric acids are obtained.

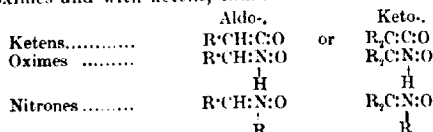
S. S. Z.

Dialkyl diarylcarbamides. H. WINKEL (U.S. Pat. 1307570).—

By conducting the reaction at 80–90°, diphenyldimethylcarbamide is prepared by passing carbonyl chloride directly into a mixture of methylaniline and dimethylaniline (which may also contain small quantities of aniline) without the use of a solvent. Aniline, methylaniline, and dimethylaniline may be mixed, in the proportions of 10, 40, and 50 parts respectively, and this mixture treated with carbonyl chloride until conversion of the methylaniline into diphenyldimethylcarbamide is completed as indicated by cessation of absorption of carbonyl chloride. The reaction mixture is then treated with dilute hydrochloric acid for the removal of dimethylaniline, and the product remaining is washed free from acid with water. It may then be further purified by crystallisation from any suitable solvent.

CHEMICAL ABSTRACTS.

Nitrones and Nitrenes. H. STAUDINGER and KARL MIESCHER (*Helv. Chim. Acta*, 1919, 2, 554–582).—In connexion with his well-known studies of compounds with “twin bonds,” Staudinger now describes several reactions of nitrones and a new class, the nitrenes. Nitrones are comparable in structure with the tautomeric forms of oximes and with ketens, thus:



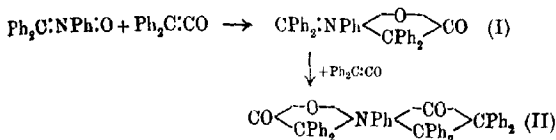
and nitrenes are comparable with allenes, thus: allenes, $R_2C:C:CR_3$; nitrenes, $R_2C:N:CR_3$. The simple nitrones are produced by the

alkylation of oximes, or by the action of aldehydes on *N*-substituted hydroxylamines. They are often formulated as cyclic ethers, thus, $R\cdot CH \begin{array}{c} \diagup NR \\ \diagdown O \end{array}$, although the evidence in favour of the nitrone formula

(the name was proposed by Pfeiffer, A., 1916, i, 327) has become very strong in recent years (compare Forster and Holmes, T., 1908, 93, 244; Brady, T., 1914, 105, 2104; Semper and Lichtenstadt, A., 1918, i, 437). It is now found that the “keto” nitrones, $R_2C:NR:O$, are readily obtained by the action of aliphatic diazo-compounds on nitroso-compounds, the reaction being represented by the following scheme, although no intermediate products have

been isolated: $R\cdot NO + R_2C \begin{array}{c} \diagup N \\ \diagdown \end{array} \rightarrow RN \begin{array}{c} O-N \\ \diagdown \diagup \\ CR_2 \end{array} \rightarrow RN \begin{array}{c} O \\ \diagdown \\ CR_2 \end{array} = R_2C:NR:O$. The presence of two double linkings in these nitrones

is revealed by the fact that they combine with diphenylketen in two stages, thus:

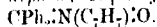


The nitrenes are formed when the products of the type I are heated, carbon dioxide being evolved. They are quite stable compounds, but capable of many reactions, of which combination with diphenylketen is particularly described.

Experiments with Diphenyldiazomethane.—Nitrosobenzene reacts with diphenyldiazomethane (A., 1916, i, 850) in ice-cold benzene to form diphenyl-*N*-phenylnitrene, $\text{CPh}_2:\text{NPh}:\text{O}$, which separates in pale yellow needles, m. p. $216-217^\circ$ (decomp.) (Angeli, A., 1911, i, 544, gives m. p. 214°). The following reactions are described: (1) hydrolysis to benzophenone and *p*-aminophenol, by boiling with dilute sulphuric acid, thus: $\text{CPh}_2:\text{NPh}:\text{O} + \text{H}_2\text{O} \rightarrow \text{CPh}_2\text{O} + \text{OH}\cdot\text{NPh} \rightarrow \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$; (2) fission by means of hydroxylamine or phenylhydrazine, benzophenone-oxime or -phenylhydrazone being formed; (3) reduction to benzophenoneanil by heating with iron powder; (4) oxidation to benzophenone and nitrobenzene by ozonising and boiling the product with water; (5) decomposition on heating, either alone or with benzene at 250° , into benzophenone, benzophenoneanil, and nitrosobenzene. The nitrene combines with phenylcarbinide (1 mol.) in benzene to form a compound, $\text{C}_6\text{H}_5\text{O}_2\text{N}_2$, m. p. $164-165^\circ$, which loses carbon dioxide at 210° and is reconverted into the nitrene by boiling with alcohol. The reaction with diphenylketen in cold benzene, in an atmosphere of carbon dioxide, results in the formation of the above pale yellow compound (I), m. p. 181° (carbon dioxide evolved), the second compound (II), a white, crystalline powder, m. p. $166-168^\circ$, being formed if the reaction is carried out in boiling benzene.

*Tetraphenyl-*N*-phenylnitrene*, $\text{CPh}_2:\text{NPh}:\text{CPh}_2$, is formed by heating compound (I) at 190° . It crystallises in small, yellow prisms, m. p. 137° , and may be reduced by aluminium amalgam in ether to *dibenzohydrilaniline*, $\text{NPh}(\text{CHPh}_2)_2$, which crystallises in silvery needles, m. p. $160-161^\circ$, is so feebly basic that solutions in mineral acids deposit the base on dilution, and may be synthesised by heating together benzohydrilaniline, diphenylbromomethane, and quinoline. The nitrene combines with diphenylketen to form a compound, $\text{C}_{46}\text{H}_{35}\text{ON}$, white needles, m. p. $203.5-204.5^\circ$, and with hydrogen chloride to give a compound, $\text{C}_{32}\text{H}_{26}\text{NCl}$, m. p. 163° , both products yielding the nitrene again when heated.

[With E. SCHLENKER.] Diphenyldiazomethane reacts with *p*-nitrosotoluene to give *diphenyl-*N*-*p*-tolynitrene*,



pale yellow needles, m. p. 153° (decomp.), which combines with

diphenylketen to form the compound, $\text{CPh}_2\text{:N}(\text{C}_7\text{H}_7)\text{<}\begin{smallmatrix} \text{O} \cdot \text{CO} \\ \text{CPh}_2 \end{smallmatrix}$, m. p. 161° , this decomposing at 170° into *tetraphenyl-N-p-tolyl-nitrene*, $\text{CPh}_2\text{:N}(\text{C}_7\text{H}_7)\text{:CPh}_2$, yellow crystals, m. p. 118° .

p-Nitrosodimethylaniline and diphenyldiazomethane produce *diphenyl-N-p-dimethylaminophenylnitrene*, $\text{CPh}_2\text{:N}(\text{C}_6\text{H}_4\text{:NMe}_2)\text{<}\begin{smallmatrix} \text{O} \cdot \text{CO} \\ \text{CPh}_2 \end{smallmatrix}$, as

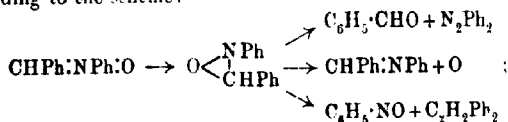
a pale yellowish-green powder, m. p. $186\text{--}187^\circ$ (decomp.). This gives a yellowish-green compound, $\text{C}_{35}\text{H}_{30}\text{O}_2\text{N}_2$, with diphenylketen, which decomposes at 169° into *tetraphenyl-N-p-dimethylaminophenylnitrene*, $\text{CPh}_2\text{:N}(\text{C}_6\text{H}_4\text{:NMe}_2)\text{:CPh}_2$, orange-yellow crystals, m. p. 155° .

Experiments with other Diazo-compounds.—Diphenylenediazomethane (*ibid.*) and nitrosobenzene produce *diphenylene-N-phenyl-nitrene*, $\begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_4 \end{smallmatrix}\text{>C:NPh:O}$, long, dark yellow needles, m. p.

$192\text{--}193^\circ$ (decomp.), its diphenylketen compound, $\text{C}_{33}\text{H}_{23}\text{O}_2\text{N}$, pale yellow, m. p. $157\text{--}158^\circ$ (decomp.), and *diphenylenediphenyl-N-*

phenylnitrene, $\begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_4 \end{smallmatrix}\text{>C:NPh:CPh}_2$, obtained as an impure, green

powder, m. p. $90\text{--}100^\circ$. Phenyldiazomethane and nitrosobenzene give *phenyl-N-phenylnitrene*, CHPh:NPh:O , m. p. $112\text{--}113^\circ$, which is the product obtained by the interaction of benzaldehyde and phenylhydroxylamine. This nitrene decomposes when heated according to the scheme:



with the exception of the stilbene, all the products have been identified. The diphenylketen compound, $\text{CHPh:NPh}\text{<}\begin{smallmatrix} \text{O} \cdot \text{CO} \\ \text{CPh}_2 \end{smallmatrix}$, is a

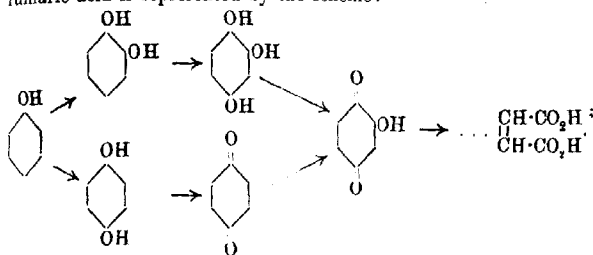
white powder, m. p. $186\text{--}190^\circ$, which decomposes on heating at 215° into *triphenyl-N-phenylnitrene*, CHPh:NPh:CPh_2 , pale yellow crystals, m. p. $105\text{--}106^\circ$, but also suffers rearrangement to a certain extent into a product, m. p. 223° , probably represented by the formula $\text{NPh}\text{<}\begin{smallmatrix} \text{CHPh:CPh}_2 \\ \text{O} \text{---} \text{C} \end{smallmatrix}$.

Ethyl diazoacetate and nitrosobenzene only react slowly and give a viscous, reddish-yellow oil, which decomposes on distillation in a vacuum into ethyl glyoxylate and azobenzene. J. C. W.

Electrochemical Oxidation of Phenols and Cresols.

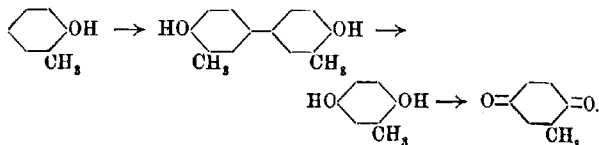
FR. FICHTER and FRANZ ACKERMANN (*Helv. Chim. Acta*, 1919, 2, 583--599).—A continuation of previously published work on the electrochemical oxidation of phenol (Fichter and Stocker, A., 1914, i, 946). It has been shown that the electrochemical oxidation of phenol produces *o*/*p*-diphenol and *pp*/*p*-diphenol, which are inter-

mediate products in the formation of quinol and catechol. In the present experiments, 5.5 grams of catechol dissolved in 60 c.c. of 0.5*N*-sulphuric acid were subjected to a current of 0.02 amp./cm.² between lead electrodes. When no diaphragm was used, the products consisted of carbon dioxide, carbon monoxide, a volatile liquid with an odour of butyric acid, which consists of a mixture of butyric acid and its lower homologues, particularly formic acid, and succinic acid. When a diaphragm is used, the product consists of fumaric acid. The electrochemical oxidation of phenol to fumaric acid is represented by the scheme:

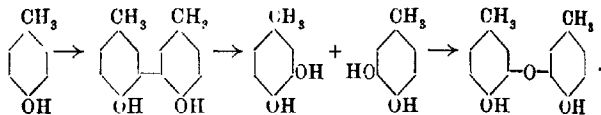


A number of experiments are described in which an attempt is made to ascertain the relative quantities of catechol and quinol produced in the electrochemical oxidation of phenol. By means of *E.M.F.* measurements, it is shown that at low concentrations quinol is a more active depolariser of a platinum electrode in 2*N*-sulphuric acid than catechol, but at concentrations above 0.05*N* the relationship is reversed. In a neutral solution, phenol has no depolarising action, and catechol has a much stronger depolarising action than quinol. In the case of a lead dioxide anode, catechol is much the strongest depolariser, so that the results allow no conclusion to be drawn as to the ratio of the two substances formed. An estimation of the amount of carbon dioxide formed in the electrolysis of phenol, catechol, and quinol, respectively, leads to the result that approximately the same quantities of quinol and catechol are formed in the electro-oxidation of phenol. An attempt to estimate directly the amount of quinol formed yielded no definite result, chiefly because of the presence of a resin in the products. The formation of the fatty acids is due to a reduction of the catechol, followed by an oxidation of the product of reduction. The reduction product of catechol is shown in a separate experiment to be *cyclohexanol*. This can be prepared by reducing a solution of 2.2 grams of catechol in 50 c.c. of 2*N*-sulphuric acid in a large platinum crucible with the anode in a porous pot. The high boiling residue of the electro-oxidation of phenol is shown to consist of diphenols, *o*-hydroxyphenyl ethers, diphenyl, tetrahydroxydiphenyl, and a dihydroxydiphenyl ether of the formula $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$. The electro-oxidation of *o*-cresol (540 grams in 2½ litres of *N*-sulphuric acid) by a current of anode density 0.0025 amp./sq. cm. without diaphragm and with vigorous

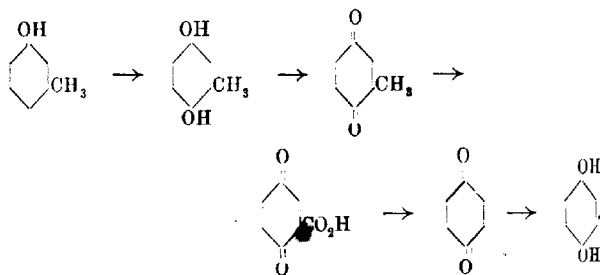
stirring gave, after 135.3 amp. hours had been passed, a dark brown oil and an aqueous solution. The oil consisted of *o*-dicresol, and the aqueous solution contained 2:5-toluquinone. The present results, together with previous work, show that the electro-oxidation of *o*-cresol may be represented by the scheme:



Similar experiments with *p*-cresol yielded from the aqueous layer toluquinone and benzoquinone, whilst the oily layer gave *p*-dicresol and 2:2'-dihydroxy-5:5'-dimethyldiphenyl ether. The formation of the latter compound is regarded as due to the loss of a molecule of water from two molecules of homocatechol. The electro-oxidation of *p*-cresol is represented by the scheme:



The formation of 2:5-toluquinone and *p*-benzoquinone in the present case is attributed to the presence of *m*-cresol in the material used. The oxidation scheme for *m*-cresol is represented as follows:



J. F. S.

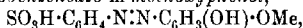
Certain Amino- and Acylamino-phenol Ethers. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1919, **41**, 1450—1472).—DERIVATIVES OF PHENOL AND *o*- AND *m*-CRESOL.—Chloroaceto-*o*-anisidide, from the base by the method already described (*A.*, 1917, i, 552), has m. p. 48.5—49° (corr.). Chloroaceto-*m*-anisidide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, forms tufts of flat needles, m. p. 90.5—91° (corr.). Chloroaceto-*o*-phenetidide crystallises in hexagonal rhombs, m. p. 65.5—67.0° (corr.), and chloroaceto-*m*-phenetidide in glistening, flat needles, m. p.

125.5—126.5°. *Aceto-4-methoxy-m-toluidide*, large, nacreous scales, m. p. 103—103.5°, from 5-amino-*o*-cresol (A., 1917, i, 695) by acetylation and then methylation with methyl sulphate, is hydrolysed by boiling hydrochloric acid (1:1) to 4-methoxy-*m*-toluidine, m. p. 59—59.5° (Bamberger, A., 1912, i, 691), and then converted into *chloroaceto-4-methoxy-m-toluidide*, delicate needles, m. p. 90—92°. 4-Methoxy-*o*-toluidine, m. p. 13—14° (corr.), b. p. 146—147°/23 mm. (*ibid.*), is obtained by the methylation and subsequent hydrolysis of 6-acetylaminio-*m*-cresol (A., 1917, i, 695), and converted into *chloroaceto-4-methoxy-o-toluidide*, which forms hair-like needles, m. p. 134.5—135.5°. 3-Nitro-*p*-anisidine, obtained by nitrating aceto-*p*-anisidine and hydrolysing the product, crystallises in orange-red prisms and plates, m. p. 57—57.5° (corr.), and 3-nitro-4-methoxychloroacetanilide forms golden-yellow, flat needles, m. p. 149.5—151.5°. *p*-Anisidine is sulphonated and then acetylated, yielding 3-acetyl-amino-6-methoxybenzenesulphonic acid, flat needles, which intumesce at 197—198°, then resolidify, and finally melt at 250° (decomp.). The crude sodium salt of this acid is ground with phosphorus pentachloride, and the product is converted into the *sulphonamide*, m. p. 233—235.5° (not purified), which is hydrolysed by dilute hydrochloric acid to 3-amino-6-methoxybenzenesulphonamide, radiate aggregates of creamy spindles, m. p. 184.5—186°.

DERIVATIVES OF THE ETHERS OF 4-AMINOCATECHOL.—3:4-Methylenedioxychloroacetanilide forms microscopic needles, m. p. 157.5—158.5°. 4-Aminoguaiacol (this vol., i, 265) yields 4-hydroxy-3-methoxychloroacetanilide in pale pink, nacreous plates, m. p. 113—114°. 3-Hydroxy-4-methoxychloroacetanilide also forms pale pink, nacreous plates, m. p. 140—150°. *o*-Ethoxyphenol is coupled with diazotised sulphanilic acid, and the dye, *p*-sulphobenzenearso-ethoxyphenol, dark red plates with 2H₂O, is reduced by means of ammonium sulphide to 4-amino-6-ethoxyphenol (4-hydroxy-5-ethoxyaniline), which crystallises in minute, hexagonal plates, m. p. 186—188°. This base yields 4-hydroxy-5-ethoxyacetanilide, nacreous plates, m. p. 165.5—166.5°, and the *chloroacetanilide*, OEt·C₆H₄(OH)·NH·CO·CH₂Cl, woolly needles, m. p. 155—156°. 3:4-Dimethoxychloroacetanilide, long, silky needles, m. p. 133.5—134.5°, is obtained from 4-aminoveratrole. 4-Acetylaminoguaiacol is ethylated by means of ethyl sulphate, giving 3-methoxy-4-ethoxyacetanilide, long, narrow, nacreous plates, m. p. 148.5—150° (Freys's methoxyphenacetin? A., 1901, i, 321). This is hydrolysed to 3-methoxy-4-ethoxyaniline, prismatic needles, m. p. 55° (corr.), b. p. 175—176°/20 mm., and then converted into the *chloroacetanilide*, long, silky needles, m. p. 133—134°. The above 4-hydroxy-5-ethoxyacetanilide is methylated and converted into 4-methoxy-5-ethoxyacetanilide, very thin, faintly purple scales, m. p. 145—146°. 4-methoxy-5-ethoxyaniline, faintly pink, rhombic crystals, m. p. 81.5—82° (corr.), and the *chloroacetanilide*, woolly needles, m. p. 135.5—136°. The same compound, on ethylation, yields 3:4-diethoxyacetanilide, m. p. 124—125.5° (Wisinger.

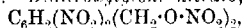
A., 1901, i, 205), from which 3:4-diethoxyaniline, creamy prisms, m. p. 47·5—48·5°, and 3:4-diethoxychloroacetanilide, m. p. 122·5—124·5°, may be obtained.

DERIVATIVES OF THE ETHERS OF RESORCINOL.—Resorcinol monomethyl ether is coupled with diazotised sulphanilic acid, and the dye, *p*-sulphobenzeneazo-*m*-methoxyphenol,



lustrous, brownish-orange platelets, with $1\text{H}_2\text{O}$, a brick-red powder, decomp. 250°, when dried, is reduced to 4-amino-5-methoxyphenol (4-hydroxy-6-methoxyaniline), pale purplish-brown needles, m. p. 175—180° (the hydrochloride is described by Henrich and Rhodius, A., 1902, i, 447). The base is converted into 4-hydroxy-6-methoxyacetanilide, pale pink aggregates of minute needles, m. p. 169—171·5°, and the chloroacetanilide, nacreous platelets, m. p. 165·5—166·5°. *p*-Sulphobenzeneazo-*m*-ethoxyphenol, flat, brownish-orange needles, with $1\text{H}_2\text{O}$, or a brick-red powder when dried, is obtained from resorcinol monoethyl ether and converted into 4-amino-5-ethoxyphenol (4-hydroxy-6-ethoxyaniline), grey, microscopic leaflets, m. p. 152—154°, 4-hydroxy-6-ethoxyacetanilide, pointed prisms, m. p. 172·5—174·5°, and the chloroacetanilide, feathery aggregates, m. p. 158·5—161°. 2:4-Dimethoxyaniline, m. p. 32·5—33·5°, is obtained from 4-hydroxy-2-methoxyacetanilide (compare Bechhold, A., 1889, 1155) and converted into 2:4-dimethoxychloroacetanilide, slender needles, m. p. 89·5—90° (corr.). The same compound is also ethylated, and thus made the source of 2-methoxy-4-ethoxyacetanilide, pale pink, glistening platelets, m. p. 117·5—118·5°, 2-methoxy-4-ethoxyaniline, faintly pink rhombs, m. p. 27·5—28·5° (corr.). *b* p. 151·5—152·5°/12 mm., and the chloroacetanilide, flat, narrow, striated plates, m. p. 97·5—98°. The above 4-hydroxy-6-ethoxyacetanilide is methylated or ethylated, and converted in turn into 4-methoxy-6-ethoxyacetanilide, faintly pink, silky needles, m. p. 100·5—101°, 4-methoxy-6-ethoxyaniline, m. p. 22·5°, *b* p. 144—144·5°, the chloroacetanilide, m. p. 126—127°. 2:4-diethoxyacetanilide, 2:4-diethoxyaniline, m. p. 33·5—34° (Will and Pukall, A., 1887, 660), and 2:4-diethoxychloroacetanilide, woolly needles, m. p. 102—103° respectively. J. C. W.

Nitro-compounds for Use in Explosives. C. M. STINE (U.S. Pat. 1309551).—Dinitroxyglylene nitrate,

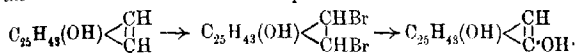


is produced by chlorinating xylene at 100° in sunlight until an increase in weight corresponding with the formation of the dichloro-derivative has been attained, cooling the reaction mixture to obtain a mass of crystals of *p*-xylylene chloride, and, after filtration, nitrating them with a mixture of nitric and sulphuric acids until a dinitro-derivative is obtained; this is heated with water under a pressure of 20 lb. per sq. in. until the chlorine has been replaced by the hydroxyl group, then evaporating the aqueous solution to expel water and hydrochloric acid, and obtain dinitro-*p*-xylylene hydroxide in well-defined crystals which are further nitrated. The

final product is a white, crystalline substance, which is stable and constitutes a powerful explosive. The following substances are also mentioned as capable of similar production and use: *dinitroxylyl nitrate*, *nitrohydroxyxylylene nitrate*, *dinitrohydroxyxylylene nitrate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{CH}_2 \cdot \text{O} \cdot \text{NO}_2)_3$, $\text{C}_6\text{HMe}(\text{NO}_2)_2(\text{CH}_2 \cdot \text{O} \cdot \text{NO}_2)_2$.

CHEMICAL ABSTRACTS.

Hydroxycholesterol. III. I. LIFSCHUTZ (*Zeitsch. physiol. Chem.*, 1919, **106**, 271—296. Compare A., 1914, i, 683; 1916, i, 558).—Cholesterol dibromide, prepared by brominating cholesterol, gives up a part of its bromine on heating with acetic acid. The bromine is removed from the dibromide more readily by boiling with water. By boiling for some time in the presence of sodium acetate in a reflux condenser it may be removed entirely, giving rise to a mixture which is partly amorphous and partly crystalline. The spectrum analysis and other reactions show that the amorphous product is hydroxycholesterol, identical with the compound obtained by the oxidation of cholesterol. The formation of hydroxycholesterol from the dibromide of cholesterol is represented as follows:



The double bond of the cholesterol eliminated by the bromination is thus re-established.

The crystalline substance, m. p. 139—141°, is a modified cholesterol, for which the author proposes the name of *metacholesterol*. A similar substance is prepared directly from cholesterol by oxidation. Mineral acids have the same effect on cholesterol dibromide as water, only the reaction is more vigorous.

On boiling cholesterol dibromide with dilute aqueous potassium hydroxide, hydroxycholesterol as well as the unchanged dibromide is obtained. Alcoholic potash, on the other hand, produces a substance which shows the properties of a hydroxy-derivative of cholesterol, but is not identical in its properties with the known hydroxycholesterol. The author names this substance *isohydroxycholesterol*. Details are further given of the bromination of hydroxycholesterol.

S. S. Z.

Crystallography of Phenyl Benzoate. MARIA STURA (*Riv. Min. Crist. Ital.*, 1917, **48**, 86—90).—This compound is monoclinic; complete crystallographic data are given. CHEMICAL ABSTRACTS.

Action of Cyanogen Bromide on Aromatic Hydrocarbons under the Influence of Aluminium Chloride. P. KARRER and E. ZELLER (*Helv. Chim. Acta*, 1919, **2**, 482—486).—When aromatic hydrocarbons are mixed with finely powdered aluminium chloride and freshly prepared cyanogen bromide and subsequently warmed until evolution of halogen hydrides ceases, good yields of nitriles are obtained. Toluene gives *p*-toluonitrile with a very little of the *o*-nitrile, and anthracene, dissolved in carbon disulphide, gives the unknown *anthracene-9-carboxylonitrile*, m. p. 170—172°, which is

identified by hydrolysis to the known acid and oxidation to anthraquinone.

Scholl and Nörr obtained quite different results when investigating this reaction (A., 1900, i, 386). It may be that they did not use fresh cyanogen bromide, for this is essential to the production of nitriles.
J. C. W.

Preparation of Vanillin. CONFECTIONERY INGREDIENTS, LTD., FRANCIS EDWARD MATTHEWS, ALBERT THEODORE KING, and THOMAS KANE (Brit. Pat., 131161).—Acyl derivatives of 4-hydroxy-3-methoxybenzoyl chloride, such as the acetate, benzoate, or carbonic ester or the *p*-toluenesulphonic ester, and arylalkyl derivatives, such as the benzyl ether, are reduced to the corresponding vanillin derivatives when their solution in toluene, xylene, or other suitable inert solvent is subjected at boiling temperature to a current of dry hydrogen in presence of a suitable catalyst; this may consist of any metal ordinarily known to be suitable for carrying out hydrogenations or reductions in liquid media (although palladium is preferred), deposited if desired on asbestos or barium sulphate or other suitable carrier. The product of reduction is hydrolysed to vanillin. Thus a nearly theoretical yield of vanillin sodium hydrogen sulphite is obtained when dry hydrogen is passed through a boiling mixture of vanilloyl chloride *p*-toluenesulphonic ester (154 parts), dry xylene (1000 parts), and palladised barium sulphate (5%, 30 parts) until evolution of hydrogen chloride ceases.
H. W.

Benzaldoxime Peroxide. PAUL ROBIN (*Compt. rend.*, 1919, 169, 695–696).—Contrary to Beckmann's results (compare A., 1889, 980), the author finds that when benzaldoxime peroxide is boiled in benzene it decomposes, giving benzaldoxime and dibenzenyloxyazoxime. When oxidised by iodine and sodium carbonate the peroxide gives dibenzenyloxyazoxime and its decomposition products.
W. G.

Hydroxy-carbonyl Compounds. II. Synthetic Experiments in the Filix Group. P. KARRER (*Helv. Chim. Acta*, 1919, 2, 466–481. Compare this vol., i, 160).—The extract of male fern root (*Aspidium filix mas*), which is the favourite remedy against the tape-worm, contains a number of active principles which have been investigated by Boehm (A., 1898, i, 40; 1899, i, 32, 804; 1902, i, 36, 37). These are all butyryl derivatives of phloroglucinol ethers, aspidinol having one benzene nucleus, albaspidin and flavaspidic acid having the structure of diphenylmethane, and filixic acid that of triphenylmethane. With the exception of the alkaloids of the pomegranate root, all other known tænia drugs are also butyric or isobutyric acid derivatives. It is, therefore, of interest to synthesise simple butyrôphenones in order to test their physiological action. In addition, many indications have been received that the activity of related substances is greater the fewer the number of methyl

groups which are present as substituents in the nuclei. For example, tryptaflavine is more active than acridine yellow, salvarsan than its dimethyl derivative, and cignolin than chrysarobin. Consequently, the aim in the present synthesis is to obtain butyrophenone derivatives with as few methyl groups as possible. Hoesch's method has again proved successful, the butyronitriles condensing quite readily with phloroglucinol derivatives in the presence of hydrogen chloride and zinc chloride.

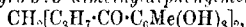
Phlorobutyrophenone [2:4:6-trihydroxyphenyl propyl ketone] crystallises in long needles with $1\text{H}_2\text{O}$, which lose water at 110° and then have m. p. $179\text{--}180^\circ$. It gives an intense red colour with ferric chloride, and couples with diazoaminobenzene to form 2:4:6-trihydroxy-3:5-dibenzeneazophenyl propyl ketone, in felted masses of orange-red needles, m. p. $136\text{--}137^\circ$. *Phloroisobutyrophenone* [2:4:6-trihydroxyphenyl isopropyl ketone] also crystallises with $1\text{H}_2\text{O}$ in white needles, m. p. $177\text{--}178^\circ$ (mixed m. p. 174°).

Methylphloroglucinol is prepared by dissolving phloroglucinol in water, adding hydrochloric acid and formalin, and reducing the precipitate of hexahydroxydiphenylmethane with zinc dust and sodium hydroxide. It reacts as above to form *methylphlorobutyrophenone* [2:4:6-trihydroxy-m-tolyl propyl ketone], which crystallises with $1\text{H}_2\text{O}$, m. p. $154\text{--}155^\circ$, and gives a violet colour with ferric chloride. Dimethylphloroglucinol yields *dimethylphlorobutyrophenone* (2:4:6-trihydroxy-m-5-xylol propyl ketone), which is less soluble than the isomerides, crystallises in anhydrous, felted needles, m. p. 140° , and gives a dirty, yellowish-brown colour with ferric chloride.

Phloroglucinol monomethyl ether gives the two isomeric phlorobutyrophenone methyl ethers. One is more soluble in light petroleum and less soluble in water than the other, and these are sufficient reasons for supposing that this one has the ketone group opposite the methoxyl group, that is, it is 2:6-dihydroxy-4-methoxyphenyl propyl ketone; it crystallises in pale yellow leaflets, m. p. 113° . The isomeride, 2:4-dihydroxy-6-methoxyphenyl propyl ketone forms pure white needles, m. p. 130° .

Methylphloroglucinol *p*-methyl ether yields 2:4-dihydroxy-6-methoxy-m-tolyl propyl ketone, in white needles, m. p. $151\text{--}5^\circ$. Aspidinol, m. p. $156\text{--}160^\circ$, is the 4:6-dihydroxy-2-methoxy-derivative, and therefore the synthetic ketone is designated *isoaspidinol*.

Methylphlorobutyrophenone condenses with formaldehyde in the presence of dilute sodium hydroxide to form 2:4:6:2':4':6'-hexahydroxy-5:5'-dibutyl-3:3'-dimethyldiphenylmethane,



which crystallises in microscopic needles, m. p. 212° . Phlorobutyrophenone and phloroisobutyrophenone also condense with formaldehyde to form such compounds, but owing to the free position in the nuclei, further condensations take place to a certain extent and the products are impure.

The naturally occurring filix compounds are more active the more complex they are, but of the above synthetic products the unicyclic ones are more active than the diphenylmethane representatives.

Phloroisobutyrophenone, which so closely resembles its isomeride in m. p. and chemical properties, has about twice its activity.

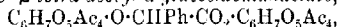
J. C. W.

Hydroxy-carbonyl Compounds. III. Synthesis of *iso*-Cotoin. P. KARRER (*Helv. Chim. Acta*, 1919, 2, 486—489).—With the hope of synthesising cotoin (2:6-dihydroxy-4-methoxybenzophenone), the active ingredient of coto-bark, Hoesch's method has been applied to phloroglucinol monomethyl ether and benzonitrile. The only product which could be isolated, however, and this in good yield, is isocotoin [2:4-dihydroxy-6-methoxybenzophenone], which crystallises from water in yellow needles, m. p. 162° (cotoin has m. p. 131°). It seems to be the rule that ketones of this type, with the methoxyl group adjacent to the ketone group, are more soluble in water and less soluble in light petroleum than their isomerides with a *p*-methoxyl group [compare paeonol and isopaeonol, acetovernone and isoacetovernone (A., 1915, i, 820), and the phlorobutyrophenone methyl ethers (preceding abstract)].

Piperonylonitrile forms a *double compound* with zinc chloride, $\text{CH}_2\text{O}_5\text{C}_6\text{H}_3\text{CN}\cdot\text{ZnCl}_2$, which crystallises in slender needles, m. p. 157—158°, and therefore cannot be used in Hoesch's synthesis.

J. C. W.

Glucosides. IV. The Glucosides of Mandelic, Lactic, and Salicylic Acids. A New Chemical Resolution of Mandelic Acid. P. KARRER, C. NÄGELI, and H. WEIDMANN (*Helv. Chim. Acta*, 1919, 2, 425—436. Compare this vol., i, 338).—Besides the tetra-acetylglucosidomandelic acids and the tetra-acetylglucose mandelates which are formed when the silver salts of active and inactive mandelic acids are treated with acetobromoglucose, *l*-mandelic acid, and this isomeride only, gives a *tetra-acetyl-d-glucose β-tetra-acetyl-d-glucosidomandelate*,



in snowy crystals, m. p. 235°, $[\alpha]_D^{25} -74.96^\circ$ (in chloroform). A separation of the three products is effected as follows. The tetra-acetylglucosidomandelate remains in solution in the toluene on cooling the reaction mixture, whilst the new ester and the tetra-acetylglucose mandelate separate. The new ester is almost insoluble in alcohol, and may thus be freed from the tetra-acetylglucose mandelate. Starting with inactive mandelic acid, a clear separation of the active components may thus be effected. The different behaviour of the two acids may be explained on steric grounds; it is possible that in the *d*-acid the hydroxyl groups are so near together that there is only room for one tetra-acetylglucose residue at a time, thus:



If this is so, then inactive acetobromoglucose should effect the same separation, and the authors are collecting the necessary material for such an investigation.

More complete directions are given for the preparation, from the tetra-acetyl compounds, of β -*d*-glucosido-*d*- and -*l*-mandelic acids. These crystallise with 1EtOH in slender needles. β -*d*-Glucosido-*dl*-lactic acid, a hygroscopic, snowy powder, is also more completely described.

Tetra-acetyl-*d*-glucose salicylate has $[\alpha]_D^{25} -39.50^\circ$ (in chloroform) and β -tetra-acetyl-*d*-glucosidosalicylic acid has $[\alpha]_D^{25} -28.47^\circ$ (compare A., 1917, i, 539). The latter has now been hydrolysed to β -*d*-glucosidosalicylic acid, $C_6H_4(O_2C \cdot O \cdot C_6H_4 \cdot CO_2H)$, which crystallises in radiate bundles of needles with $1\frac{1}{2}H_2O$, m. p. 142° (decomp.), $[\alpha]_D^{25} -49.25^\circ$, and may be called *salicinic acid*, because of its relationship to salicin. J. C. W.

A Simple Method of Demonstrating the Production of Aldehyde by Chlorophyll and by Aniline Dyes in the Presence of Sunlight. W. J. V. OSTERHOUT (*Amer. J. Bot.*, 1918, 5, 511—513).—For the preparation of chlorophyll for the experiments described, fresh leaves were extracted with alcohol, the alcoholic extract shaken with carbon tetrachloride, and the carbon tetrachloride, after separation, sprayed on to filter paper and allowed to evaporate. After spraying the paper several times, it acquired a deep green colour. A bell jar was lined with such filter paper, moistened with water, and then inverted over a small dish of water, sealed from the air and exposed to sunlight. When the paper was bleached to a pale green colour, the water in the dish generally gave a positive test for aldehydes, indicating the formation of a volatile aldehyde. The result was the same whether carbon dioxide was entirely excluded from the air in the jar or whether its concentration was increased to 10%. This supports the view that the aldehyde is not produced by the decomposition of carbon dioxide, but rather by the decomposition of the chlorophyll.

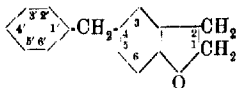
Similar results were obtained when a number of aniline dyes, particularly methyl-green and iodine-green, were used in place of chlorophyll. W. G.

Syntheses in the Catechin Group. P. KARRER and FR. WIDMER (*Helv. Chim. Acta*, 1919, 2, 454—465).—Compounds of

the type of catechin, $C_6H_3(OH)_2 \cdot CH(OH) \cdot C_6H(OH)_2 \leftarrow \begin{array}{c} CH_2 \cdot CH_2 \\ | \\ O \end{array}$,

are widely distributed in nature, but the only syntheses which have been effected in this series are due to Kostanecki and his pupils; they are very complicated, and so far have only furnished methyl ethers of the desired products. A simple method has now been discovered. Hydroxycoumarones or hydroxycoumarans are condensed with nitriles under the influence of hydrogen chloride, and the ketimides so formed are boiled with water, giving ketones which are easily reduced to the required secondary alcohols. The method is, in effect, another application of Fieser's synthesis of phenolic ketones (A., 1915, i, 820; 1917, i, 342).

It is proposed to call the parent 4-benzylcoumaran "depsan," and the coumarone derivative "depsen," with depsanone and depsenone for the ketones, and depsanol and depsenol for the secondary alcohols, the notation being as in the annexed formula.

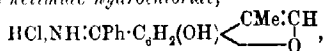


Resorcinol and ethyl chloroacetate are condensed in the presence of sodium ethoxide to ethyl *m*-hydroxymethylcoumarilate, m. p. 178°, which is hydro-

lysed to the free acid, m. p. 226° (evolution of carbon dioxide). The dry acid is heated at 180–190°, when 5-hydroxy-2-methylcoumarone is obtained as a sublimate of white needles, m. p. 103°, which may be preserved for a long time. This mode of preparation is an improvement on that of Hantzsch (A., 1887, 262) or Pechmann (A., 1901, i, 211). The coumarone exhibits sky-blue fluorescence in alkaline solutions, and gives a brownish-red coloration with alcoholic ferric chloride, which changes to blue on diluting with water. By reduction with sodium and alcohol, it yields 5-hydroxy-2-methylcoumaran, $\text{OH} \cdot \text{C}_6\text{H}_5 \text{ < } \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{O} \end{array}$, which

sublimes or crystallises in white needles, m. p. 96°.

5-Hydroxy-2-methylcoumarone is dissolved in ether, mixed with a little zinc chloride and an equivalent quantity of benzonitrile, and the whole submitted to a current of dry hydrogen chloride for six hours. The ketimide hydrochloride,



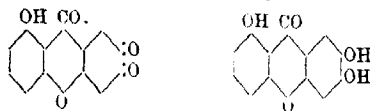
which separates in bundles of pale green crystals, m. p. 77°, is boiled with water, and thus hydrolysed to 5-hydroxy-2-methyldepsenone (5-hydroxy-4-benzoyl-2-methylcoumarone). This crystallises in slender, golden-yellow forms, m. p. 158°, gives an intensely yellow sodium salt, and may be methylated by methyl sulphate. 5-Methoxy-2-methyldepsenone forms stout, pale yellow crystals, m. p. 79°, and does not reduce permanganate. This is important, as it shows that the furan ring of the original coumarone has not been ruptured during the condensation with the nitrile. Reduction of the ketone to the hydrol is effected by zinc dust and 5% sodium hydroxide. 5-Hydroxy-2-methyldepsenol forms bundles of small, very pale pink crystals, m. p. 141°.

5-Hydroxy-2-methyldepsanone, small, sulphur-yellow needles, m. p. 159°, giving a green coloration with alcoholic ferric chloride, and 5-hydroxy-2-methyldepsanol, slender, pale pink needles, m. p. 152° (turns dark brownish-red at 100°), are obtained in the same way from 5-hydroxy-2-methylcoumaran. J. C. W.

Correction of an Error Relating to a Trihydroxyxanthone.

A. L. VAN SCHERPENBERG (*Chem. Weekblad*, 1919, 16, 1146–1149). —When euxanthone is oxidised with chromic acid, a red substance is obtained to which the constitution 2-hydroxy-5:8-quinoxanthone has been assigned (Nierenstein, A., 1913, ii, 382). Reduction of

this compound with zinc in acetic acid gives a yellow substance of the corresponding structure, 2:5:8-trihydroxyxanthone. The following arguments, based on the experimental results of Nierenstein, are advanced by the author against the adoption of this view. The red substance, on treatment with nitric acid, gives trinitroresorcinol, indicating the presence of a resorcinol residue not accounted for by the above formulation. Attempts to acetylate, benzoilate, and alkylate the quinone substance were not successful. This accords with the view that the hydroxyl group occupies the 8-position, and not the 3-position. The yellow reduction product melts with decomposition, a property of hydroxyxanthones with a hydroxyl group in the 3- or 6-position. The formulation of the two substances as 8-hydroxy-2:3-quinoxanthone and 2:3:8-trihydroxyxanthone, respectively, is therefore proposed.



W. S. M.

δ-Cinchonine and its Isomerides; its Relations to Niquine.

E. LÉGER (*Compt. rend.*, 1919, **169**, 797—800).—By fractional crystallisation of its hydrochloride from alcohol, it is now shown that the δ-cinchonine previously described by Jungfleisch and Léger (compare A., 1894, i, 262) is really a mixture of two isomerides, which the author names *α-cinchonhydrine* and *β-cinchonhydrine*. These substances have respectively m. p. 144.4° and 155.8°. $[\alpha]_D +196.8^\circ$ and $+106^\circ$ (in water with 2HCl), $[\alpha]_D +139.8^\circ$ and $+72.16^\circ$ (in alcohol). These figures indicate that the δ-cinchonine described by Langer (compare A., 1911, i, 403) is identical with the *α-cinchonhydrine* now described. With each of these bases, acetic anhydride gives a diacetyl derivative, from which the original base can be regenerated unchanged.

When heated for twenty-four hours with 50% sulphuric acid, *α-cinchonhydrine* is converted into *γ-cinchonhydrine*, which has $[\alpha]_D +140.2^\circ$.

It is suggested that the cinchonhydrines bear the same relationship to cinchonine as niquine does to hydroquinine. W. G.

The Crystallography of Morphine and certain of its Derivatives. EDGAR T. WHERRY and ELIAS YANOVSKY (*J. Washington Acad. Sci.*, 1919, **9**, 505—513).—Attempts have been made to apply the optical-crystallographic method devised for the identification of the cinchona alkaloids (A., 1918, ii, 339) to the morphine group of alkaloids and the crystallographic and optical properties of a number of these have been studied. Owing to the ready solubility, however, of these substances in every immersion liquid approaching them in refractive index, the method is impracticable.

Morphine monohydrate, $C_{17}H_{19}O_3N \cdot H_2O$, was obtained in good crystals from methyl alcohol: rhombic bisphenoidal [$\alpha:b:c=0.499:1:0.927$]; refractive indices, α 1.580, β 1.625, γ 1.645. D 1.32; M.V. 229.7.

Codeine (morphine methyl ester), $C_{18}H_{21}O_3N$, was crystallised from ethyl acetate: rhombic bisphenoidal [$\alpha:b:c=0.931:1:0.509$]; double refraction positive, dispersion strong. D 1.32; M.V. 226.7.

Codeine monohydrate, $C_{18}H_{21}O_3N \cdot H_2O$, was crystallised from water and from aqueous methyl alcohol: rhombic, probably bisphenoidal [$\alpha:b:c=0.960:1:0.830$]; double refraction negative, dispersion distinct. D 1.31; M.V. 242.1.

Codethyline (morphine ethyl ester monohydrate), $C_{19}H_{23}O_3N \cdot H_2O$, crystallised from ether in prisms: rhombic, probably bisphenoidal [$\alpha:b:c=1.454:1:0.789$]; double refraction positive, dispersion distinct. D 1.29; M.V. 256.7.

Heroin (diacetylmorphine), $C_{21}H_{23}O_5N$, was obtained in excellent crystals from ethyl acetate: rhombic bisphenoidal [$\alpha:b:c=0.8952:1:0.497$]; double refraction negative, dispersion strong. D 1.32; M.V. 279.7.

The relations between the topic parameters of the crystals are discussed.
E. H. R.

Addition Reactions and Ring Fission of certain Heterocyclic Compounds. SIEGFRIED SKRAUP (*Annalen*, 1919, 419, 1—92).—The behaviour of various heterocyclic compounds towards hydroxylamine has been investigated; the results are interpreted with the aid of Werner's theory of the varying affinity values of simple bonds.

Ethyl 2:4:6-trimethyldihydropyridine-3:5-dicarboxylate reacts with hydroxylamine hydrochloride in boiling absolute methyl alcoholic solution to yield ammonium chloride, ethyl 2:4:6-trimethylpyridine-3:5-dicarboxylate, and 4-ethylidenebis-3-methyl-5-*iso*-oxazolone, $O \begin{smallmatrix} \diagup & \text{CO} \cdot \text{CH} - \text{CHMe} - \text{CH} \cdot \text{CO} \\ \diagdown & \text{N} = \text{CMe} \end{smallmatrix} \begin{smallmatrix} \text{MeC} = \text{N} \\ \diagup \end{smallmatrix} > O$, m. p. 156° (compare

Rabe, A., 1904, i. 509). The primary product of the action appears to be ethyl ethylidenebisacetoacetate, which then yields the *isooxazolone* on the one hand and the pyridine derivative on the other hand through the intermediate formation of a *N*-hydroxy ring compound. In support of this hypothesis, it is found that small quantities of ethyl trimethylpyridinedicarboxylate are formed by the action of hydroxylamine hydrochloride on ethyl ethylidenebisacetoacetate. Under similar conditions, ethyl 2:6-dimethyldihydropyridine-3:5-dicarboxylate yields ethyl 2:6-dimethylpyridine-3:5-dicarboxylate in 20% yield, whilst a 49.5% yield of ethyl 4-phenyl-2:6-dimethylpyridinedicarboxylate, m. p. 66° (*picrate*, m. p. 148—149°), is obtained from the corresponding dihydro-compound. With ethyl 2:6-dimethylisopropylidihydropyridinedicarboxylate and ethyl 4-benzyl-2:6-dimethyldihydropyridinedicarboxylate a different but not unexpected behaviour is observed, since in each case the substituting group is eliminated and ethyl 2:6-dimethylpyridinedicarboxylate is produced.

Ethyl 2:5-dimethylpyrrole-3:4-dicarboxylate only reacts very slowly with hydroxylamine hydrochloride. The transformation of the dihydro-derivatives into the pyridine compounds can scarcely be ascribed to a direct oxidising action of hydroxylamine since, though these substances are readily oxidised by such agents as nitrous acid, sulphur, nitric and chromic acids, they are very resistant to iodine, ferric chloride in acetone solution, and to a large excess of permanganate.

A rigid proof of the relationship of dimethyldihydropyridine- and trimethyldihydropyridine-dicarboxylic esters to 1:4-dihydropyridine has not previously been given; attempts to identify the presence of an imino-hydrogen atom by acetylation were unsuccessful, but its presence could be shown with the help of magnesium methyl iodide.

Benzothiazole is transformed by hydroxylamine into 2-amino-benzothiazole, the yield being nearly quantitative; similarly, benzoxazole is converted into 2-aminobenzoxazole, m. p. 129—130°, and *o*-formylaminophenol (identified as dibenzoyl-*o*-aminophenol, m. p. 182—183°). The following substances do not react with hydroxylamine: benziminazole (the *picrate*, m. p. 225—226°; *copper salt*, $(C_7H_5N_2)_2Cu$, red precipitate; *nickel, cobalt, cadmium, and zinc compounds* are described); 1-methylbenziminazole (m. p. 66°, b. p. 286°/746 mm., conveniently prepared by the action of potassium methyl sulphate on sodium benziminazole in aqueous solution; *picrate*, m. p. 246—247°); 1-phenylbenziminazole, benzylidene-aniline, azobenzene, 1-phenylpyrazole, 2-phenyl-1:2:3-triazole, pyridine, quinoline, 2-methylbenzothiazole, 2-phenylbenzothiazole, 4:5-diphenyloxazole, 6-dimethylaminobenzothiazole.

The following 2-substituted benzoxazoles have been prepared by heating *o*-aminophenol with the requisite nitrile or amide: 2-*isobutylbenzoxazole*, almost colourless oil, b. p. 240°/748 mm., D_{17}^{20} 0.98; 2-*tert.-butylbenzoxazole*, colourless oil, b. p. 226°/748 mm., D_{17}^{20} 0.9466; 2-*n-hexylbenzoxazole*, b. p. 282—285°, m. p. 19°, D_{17}^{20} 0.944; 2-*cyclohexylbenzoxazole*, colourless crystals, m. p. 37—38°, b. p. 298°/744 mm.; 2-*benzylbenzoxazole*, pale yellow, viscous liquid, b. p. 325°/750 mm., D_{17}^{20} 1.113; 2-phenylbenzoxazole, non-fluorescent crystals, m. p. 103°; 2-*p-tolylbenzoxazole*, colourless needles, m. p. 116—117°; 2-*p-anisylbenzoxazole*, almost colourless, crystalline needles, m. p. 101°, b. p. 363°/742 mm.; 2-*a-naphthylbenzoxazole*, colourless crystals, m. p. 107°; 2-*p-chlorophenylbenzoxazole*, long, shining needles, m. p. 150°; 2-*p-bromophenylbenzoxazole*, m. p. 158—159°; 2-*styrylbenzoxazole* (?). The fission of the oxazole ring by aqueous hydrochloric acid has been studied, and reaction is shown to occur with decreasing rapidity when the substituents are arranged in the following order: benzyl, methyl, *n*-hexyl, *cyclohexyl*, *isobutyl*, *tert.-butyl*, phenyl, *p*-tolyl, *a*-naphthyl, *p*-anisyl. The results are fully discussed in the light of the theory of partial valency.

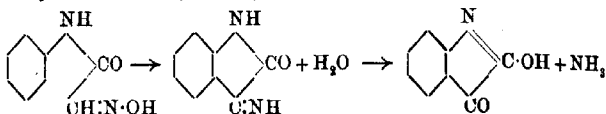
H. W.

Preparation of Isatin and its Substitution Derivatives and Intermediate Products. J. R. REIGY (Brit. Pat. 128122).—The preparation of oximinoacetanilide and its substitution products

b b*

is effected by subjecting aniline or its derivatives which are substituted in the benzene nucleus by halogens, alkyl, alkoxy, or carboxyl groups or the *N*-monoalkyl or *N*-monoaralkyl derivatives of these amines to the action of chloral hydrate in a dilute solution of a mineral acid and in the presence of hydroxylamine at a suitable temperature. Isatin and its substitution derivatives are obtained from oximinoacetanilide and its derivatives by treatment of the latter with concentrated sulphuric acid and afterwards splitting the resulting isatinimides by addition of water into isatins and ammonia. Reactions occur in accordance with the schemes

$$\text{CCl}_3\cdot\text{CH}(\text{OH})_2 + \text{NH}_2\cdot\text{OH} = \text{CCl}_3\cdot\text{CH:N}\cdot\text{OH} + 2\text{H}_2\text{O};$$

$$\text{CCl}_3\cdot\text{CH:N}\cdot\text{OH} + \text{C}_6\text{H}_5\cdot\text{NH}_2 + \text{H}_2\text{O} = \text{NHPh}\cdot\text{CO}\cdot\text{CH:N}\cdot\text{OH} + 3\text{HCl}.$$


Oximino-derivatives of the following amines have been prepared, the m. p.'s of the compounds being placed within brackets: *o*-toluidine (121°), *m*-toluidine (146°), *p*-toluidine (162°), *m*-xylylidine (161°), *p*-xylylidine (151°), methylaniline (145°), ethylaniline (160°), benzylaniline (142°), *o*-anisidine (140°), *p*-phenetidine (195°), anthranilic acid (208°), *o*-chloroaniline (150°), *m*-chloroaniline (154°), 2:5-dichloroaniline (163°), 3:4-dichloroaniline (158°), 3:5-dichloroaniline (185°), 5-chloro-*o*-toluidine (167°), 4-chloro-*o*-toluidine (148°), 6-chloro-*m*-toluidine (187°), 4-chloro-*m*-toluidine (134°), 2-chloro-*p*-toluidine (177°), 3-chloro-*p*-toluidine (188°), and *p*-bromoaniline (167°). The following isatins are described: mixture of 4- and 6-methylisatins, orange-yellow crystals, m. p. 143°; 4:7-dimethylisatin, orange-yellow crystals, m. p. 250°; 5:7-dimethylisatin, brick-red crystals, m. p. 235°; mixture of 4- and 6-chloroisatins, orange-yellow crystals, m. p. 212°; 7-chloroisatin, reddish-brown crystals, m. p. 175°; mixture of 4:5- and 5:6-dichloroisatins, yellowish-red crystals, m. p. 200°; 4:6-dichloroisatin, lemon-yellow crystals, m. p. 250°; 4-chloro-7-methylisatin, orange-yellow crystals, m. p. 273°; 5-chloro-7-methylisatin, yellowish-brown crystals, m. p. 265°; 7-chloro-4-methylisatin, orange-yellow crystals, m. p. 252°; mixture of 5-chloro-4-methyl- and 5-chloro-6-methyl-isatins, orange-yellow crystals, m. p. 200°; mixture of 4-chloro-5-methyl- and 6-chloro-5-methyl-isatin, bright red crystals, m. p. 205°; isatin-7-carboxylic acid, brownish-yellow powder, m. p. 235°. H. W.

Manufacture of *N*-Arylthiomorpholines. ROBERT ROBINSON, FRANCIS WILLIAM KAY, and BRITISH DYES, LTD. (Brit. Pat. 133108).—*N*-Arylthiomorpholines (*N*-aryltiazans) of the general formula $\text{Ar}\cdot\text{N}\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\rangle\text{S}$, applicable as intermediate products in the manufacture of dyes, may be prepared by condensing primary aromatic amines, provided they are not substituted in the ortho-position, with $\beta\beta'$ -dichloroethyl sulphide. Suitable sol-

vents, such as toluene or nitrobenzene, may be employed, and also some agent capable of neutralising hydrogen chloride, such as sodium carbonate or acetate. In some cases, as in the reaction with β -naphthylamine, copper powder may be added with advantage. A less suitable method consists in heating the base and its hydrochloride with $\beta\beta'$ -dihydroxyethyl sulphide. *N*-Phenylthiomorpholine forms flat, elongated prisms, m. p. 32° , b. p. $200^\circ/50$ mm., has an alliaceous odour, and yields a picrate, m. p. 144° . *N*-p-Tolylthiomorpholine has m. p. 35° , and the β -naphthyl derivative has m. p. about 155° .

J. C. W.

Ureides of Substituted Aminonaphtholsulphonic Acids.

B. HEYMANN, O. DRESSEL, R. KOTHE, and A. OSSENBECK (U.S. Pat. 1308071).—Ureides are produced having the general formula $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_m\text{Y}_n\cdot\text{R}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_n\text{X}_6\cdot\text{n}\cdot\text{OH})_2$, in which R stands for a bivalent group containing an acyl radicle, for example, CO, SO_2 , $\text{CO}\cdot\text{CH}\cdot\text{CH}$, $\text{CO}\cdot\text{CH}_2$, or the residue of phenylacetic acid; n is the number of hydrogen atoms remaining unsubstituted in the naphthalene ring; X is a sulphonic acid or other substituting group; m the number of unsubstituted hydrogen atoms in the benzene nucleus; and Y, substituting atoms or radicles, such as Cl, Br, Me, or OMe. These compounds form dyes when coupled with diazotised aniline or similar components, and may be employed as therapeutic agents for destroying blood-parasites. They form salts with alkali metals, alkaline earth metals, or heavy metals, for example, sodium, barium, strontium, copper, zinc, mercury, and silver, which also possess therapeutic properties. As starting materials, 1:8-aminonaphtholsulphonic acids (mono-, di-, or higher sulphonic acids) may be employed. These compounds are substituted by such nitro-compounds as *p*-nitrobenzoyl chloride, *m*-nitroanisoyl chloride, *m*-nitrobenzenesulphonyl chloride, or *m*-nitrocinnamoyl chloride. Reduction of these substituted aminonaphtholsulphonic acids is effected by the action of iron and acetic acid or other similar reducing agents, and the amino-compounds thus obtained are treated with carbonyl chloride to obtain ureides.

CHEMICAL ABSTRACTS.

Hydrazino-acids. III. AUGUST DARAPSKY (*J. pr. Chem.*, 1919, [ii], **99**, 179—231. Compare A., 1918, i, 506, 553).—The hydrazino-acids described previously have been optically inactive; the author now describes the preparation of the optically active α -hydrazinophenylacetic acids, which are prepared by the action of hydrazine hydrate on the active phenylchloroacetic acids or by the resolution of α -benzylidenehydrazinophenylacetic acid and subsequent elimination of the benzylidene group. The applicability of these acids to the study of the phenomena of the Walden inversion is limited by their tendency to complete racemisation under the experimental conditions adopted.

d- and *l*-Phenylchloroacetic acids are prepared by the resolution of the *r*-acid by means of morphine according to the method of McKenzie and Clough (T., 1908, **93**, 817; 1909, **95**, 782), and their properties agree completely with those given by these authors; the unusual experimental difficulties encountered in this resolution have

been extensively investigated, the main factors conditioning success appearing to be the slowness with which the crystals of the salt separate and the relative weight of the crop which is deposited before filtration. *d*-Hydrazinophenylacetic acid is obtained by the action of hydrazine hydrate on *l*-phenylchloroacetic acid in absolute alcoholic solution; it crystallises in shining leaflets, m. p. 183—184°, and has $[\alpha]_D^{20} + 158.02^\circ$ in *N*-hydrochloric acid solution; *l*-hydrazinophenylacetic acid, m. p. 183—184°, $[\alpha]_D^{20} - 157.64^\circ$, is similarly prepared from the *d*-chloro-acid. The acids readily condense with benzaldehyde in aqueous solution in the presence of hydrochloric acid, yielding respectively *d*- and *l*-benzylidenhydrazinophenylacetic acids, m. p. 136—138°, $[\alpha]_D^{20} + 166.40^\circ$ and -166.59° in acetone solution.

The resolution of α -hydrazinophenylacetic acid into its active components cannot be conveniently effected by means of helicine or camphor, but may be accomplished if the acidic character of the substance is increased by the introduction of suitable groups; the formyl and benzoyl groups are not applicable, since viscous syrups are formed in the first instance and difficultly decomposable compounds in the second. The benzylidene derivative can, however, be resolved by morphine in alcoholic solution. (The crystalline quinine salts of *dl*-benzylidenhydrazinophenylacetic, *dl*-*o*-hydroxybenzylidenhydrazinophenylacetic and *dl*-*p*-methoxybenzylidenhydrazinophenylacetic acids, m. p.'s 172—174°, 183°, and 161—163° respectively, are described, but are not suited for the resolution; *dl*-*p*-methoxybenzylidenhydrazinophenylacetic acid forms small, colourless needles, m. p. 131—133°.) The physical properties of the *d*-acid obtained in this manner agree completely with those of the substance prepared by the action of hydrazine hydrate on *l*-phenylchloroacetic acid and treatment of the product with benzaldehyde.

Ethyl *d*- and *l*-hydrazinophenylacetate hydrochlorides, prepared by the esterification of the corresponding acids with alcohol and hydrogen chloride, have m. p. 148—150°, $[\alpha]_D^{20} + 96.32^\circ$ and -96.30° respectively. They are converted by nitrous acid into the corresponding nitroso-esters of the same sign, but considerable racemisation occurs which appears to be attributable to the nitrous acid; this is the more remarkable since a group directly attached to the asymmetric carbon atom is not involved in the change; further extensive racemisation takes place when the crude nitroso-esters are crystallised from alcohol. On the other hand, the conversion of nitroso- into azido-ester by treatment with dilute sulphuric acid appears to occur without racemisation, and yields a product of the same sign, but it is not possible to guarantee the optical purity of these substances. When the active nitroso-esters are heated they are converted into ethyl *dl*-aminophenylacetate, racemisation being complete.

dl-Azidophenylacetic acid, m. p. 98—101° (Forster and Müller, T., 1910, 97, 138, give 98.5°), is conveniently prepared by the action of sodium azide on *r*-phenyl-chloro- or -bromo-acetic acid; when the reaction is applied to *d*-phenylchloroacetic acid, a levorotatory azido acid is obtained, which, however, is not free from mandelic acid.

Attempts to resolve *dl*-azidophenylacetic acid by quinine, quinidine, or cinchonine were unsuccessful, but partial success was attained with brucine or morphine, but the specific rotations of the acids were so low that, although the results are concordant among themselves, it is probable that the resolution was incomplete. Esterification of the azido-acids showed that racemisation unexpectedly occurs during the process, the phenomenon being more marked with alcohol and sulphuric acid than with diazoethane. Similar instances of racemisation were encountered with the active phenylchloroacetic acids, but, in these cases, the more marked effect was caused by diazoethane. Ethyl *d*-phenylchloroacetate has b. p. $138^{\circ}/19$ mm., $[\alpha]_D^{20} +121.05^{\circ}$ in alcoholic solution, but is possibly not quite free from the racemic substance. The values observed for the *l*-isomeride were b. p. $136^{\circ}/13$ mm., $[\alpha]_D^{20} -108.45^{\circ}$.

d-Hydrazinophenylacetic acid is converted by chlorine into *r*-phenylchloroacetic acid; similarly, ethyl *l*-hydrazinophenylacetate hydrochloride is transformed into slightly levorotatory ethyl phenylchloroacetate, which is not quite pure analytically. H. W.

Cause of and Remedy for certain Inaccuracies in Hausmann's Nitrogen Distribution Method. S. L. JORDI and S. C. MOULTON (*J. Amer. Chem. Soc.*, 1919, **41**, 1526—1531).—The distribution of nitrogen in casein, gelatin, and egg-albumin has been investigated. It is shown that the proportion of amide nitrogen obtained by Hausmann's method as modified by Osborne and Harris (A., 1903, i, 585) is constant, and does not depend on the quantity of magnesia added to the distillation mixture. The percentage of nitrogen contained in the magnesium oxide precipitate is higher the greater the quantity of magnesium oxide employed in distillation. Conversely, the proportion of monoamino- and diamino-nitrogen is the smaller the larger the amount of magnesia used in distillation. In order to obtain uniform results and a minimum of "humin" nitrogen it is necessary to use the least possible amount of magnesia which is sufficient to render the substance to be distilled alkaline. In the case of plant and animal materials the uniform application of 1 gram of magnesia is satisfactory, whilst in the case of proteins 0.5 gram is sufficient. J. F. S.

Identity of Hordein and Bynin. HEINRICH LÜERS (*Biochem. Zeitsch.*, 1919, **96**, 117—133).—Hordein and bynin were submitted to an analysis by the Van Slyke method, and the results obtained from the two proteins were almost identical. The author, therefore, does not agree with Osborne that bynin, which is obtained from malt, is a different protein from the hordein of barley.

S. S. Z.

Guanylic Acid, its Preparation and Precipitability. R. FEELGEN (*Zeitsch. physiol. Chem.*, 1919, **106**, 249—259).—By treating nucleoprotein from the pancreas of cattle with sodium hydroxide and precipitating with 90% alcohol in the presence of ammonium chloride, the sodium salts of guanylic and another

nucleic acid are obtained. After the purification of this mixture, sodium guanylate is obtained by precipitation with sodium acetate in the cold. Sodium hydrogen guanylate, $C_{10}H_{15}O_8N_3PNa$, is prepared by dissolving the latter in ten parts of hot water and one part of glacial acetic acid, and precipitating, after quick cooling, with three volumes of alcohol.

S. S. Z.

Urease and the Radiation Theory of Enzyme Action. I. and II. H. P. BARENDRECHT (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1126—1142, 1307—1322).—After a criticism of the hypothesis put forward by Van Slyke (*A.*, 1914, **i**, 1181), the author puts forward a new hypothesis to explain enzyme action: An enzyme acts by radiation, and the enzyme particle contains the same molecule, which is liberated or acted on by this enzyme, in some active state. The radiation by which enzymes exert their action is due to the electrons forming part of the atoms, and is of the nature of electromagnetic induction. The radiation, by which urease acts on urea, originates from the enzyme molecule, and is able to exert its hydrolytic effect to a certain distance, probably very small. When the urease radiation strikes an urea molecule, it is absorbed. The amount of urea hydrolysed in unit time by an enzyme molecule would therefore be independent of the urea concentration if the other constituents of the solution had no power of absorption of this radiation. In addition to urea, the hydrogen ions are the only constituent which absorb the radiation in this hydrolysis. At constant temperature and constant hydrogen-ion concentration, the velocity of the reaction is given by $-dx = m(x/[x + nc]) \cdot dt$, in which x is the concentration of urea, c the concentration of hydrogen ions, and n the absorption coefficient of hydrogen ions, that of urea being taken as unity. The velocity constant m for a given temperature and H^+ ion concentration is proportional to the enzyme concentration only. If a is the initial urea concentration and $(a - x)/a = y$, then, after integration, $nc/0.434 \cdot \log(1/[1 - y]) + ay = mt$. This theory is tested by experiments made on the hydrolysis of urea by extract of soja beans, and the theory generally confirmed.

In the second paper, the work is repeated, but more precautions are taken to keep the hydrogen-ion concentration constant. It is found that the value of the constant m falls off towards the end of the reaction the higher the value of P_H . For low values of P_H , the value of m increases continually from 0.03% up to 8% urea concentration. For higher values of P_H , there is first an increase and then in the most concentrated solutions of urea a decrease in the value of m . These facts are deducible from the hypothesis formulated.

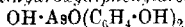
J. F. S.

The Isomeric Hydroxyphenylarsinic Acids and the Direct Arsenation of Phenol. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1440—1450).—By means of the diazo-reaction, *o*- and *m*-arsanilic acids (this vol., **i**, 50) have been converted into the phenolic acids. *o*-Hydroxyphenylarsinic

acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$, crystallises readily from hot water, being but sparingly soluble in the cold, forming rosettes of needles, m. p. 196° , and its sodium salt, $\text{C}_6\text{H}_4\text{O}_4\text{AsNa}$, separates from 50% alcohol in glistening, hexagonal platelets with $4\text{H}_2\text{O}$. *m-Hydroxyphenylarsinic acid* crystallises from a small volume of water in masses of rhombs, m. p. $159\text{--}173^\circ$, and its sodium salt, rosettes of flat needles, is extremely soluble, even in alcohol. The ortho-acid differs from its isomerides in giving a wine-red colour with ferric chloride.

A knowledge of the *o*-hydroxyphenylarsinic acid has helped in the examination of the by-products formed in the arsenation of phenol. This important reaction is carried out as follows. Arsenic acid (480 grams of 80% acid), dehydrated by heating until the temperature reaches 150° , is mixed with phenol (200) and kept gently boiling at $155\text{--}160^\circ$ for seven hours. The homogeneous product is then diluted with water (2 litres), and sufficient of a hot concentrated solution of barium hydroxide is added to render the well-stirred mixture neutral to litmus. The precipitate of barium arsenate carries with it the small amount of tarry by-product. The hot filtrate is then treated with just sufficient sulphuric acid to precipitate the barium, filtered again, and the solution evaporated under reduced pressure to about half the volume, when it is neutralised by sodium hydroxide and concentrated to a small bulk. The hot solution is mixed with several volumes of alcohol and cooled, crystallisation being induced by rubbing. Using the quantities mentioned, about 120 grams of pure sodium *p*-hydroxyphenylarsinate are obtained, without the complications of Conant's method (this vol., i, 230).

The mother liquors, when the alcohol is removed by evaporation, give the above wine-red coloration with ferric chloride. Taking advantage of the different solubilities of the barium salts and the free acids, the authors have isolated *o*-hydroxyphenylarsinic acid (14 grams). Benda's *pp'*-dihydroxydiphenylarsinic acid, m. p. $250\text{--}251^\circ$ (10 grams; A., 1908, i, 747), and an acid which is probably *op'*-dihydroxydiphenylarsinic acid,



(8 grams). The latter acid crystallises from 50% acetic acid in stout, glistening prisms, m. p. $215\text{--}217^\circ$, and gives the red colour with ferric chloride.

J. C. W.

Physiological Chemistry.

Some Conditions Influencing the Reaction Velocity of Sodium Nitrite on Blood. C. R. MARSHALL (*Proc. Roy. Soc. Edin.*, 1918–1919, **39**, 149–156).—The rate of production of methæmoglobin by the action of sodium nitrite on blood is governed

by the nature and concentration of the blood solution and by the concentration of the sodium nitrite solution. Probably other factors, such as temperature, are of importance. J. C. D.

The Role of the Plasma Proteins in Diffusion. THOMAS HUGH MILROY and JOSEPH FRANCIS DONEGAN (*Biochem. J.*, 1919, **13**, 258—271).—After severe hæmorrhage, the specific gravity, viscosity, and percentage of nitrogen in the blood fall, whilst the conductivity rises. The fluid which enters the blood after hæmorrhage must have at least the electrolyte concentration of normal plasma, since there is no evidence of a fall in conductivity. It is evident from studies of diffusion of sodium chloride from solution in water, gum arabic solution, and blood serum that some factor other than viscosity is concerned in the diffusion of salt from serum. This point was studied further, and it is concluded from the results that the globulin may exert a determining factor governing the rate of diffusion. J. C. D.

Precipitation Structures Simulating Organic Growth. II. Physico-chemical Analysis of Growth and Heredity. R. S. LILLIE and E. N. JOHNSTON (*Biol. Bull.*, 1919, **36**, 225—273. Compare Lillie, A., 1918, i, 278).—If a piece of fine iron wire, wound round one end of a fine copper wire, is dropped into a 2% solution of egg-albumin containing 4% of potassium ferricyanide and 4% or more of sodium chloride, the entire surface of the iron wire rapidly becomes covered with fine, filamentous growths. They are characteristically regular in form; the majority are straight or slightly curved, and cease to grow at a length of 200 microns or less. A repetition of this experiment, using a 2% solution of egg-albumin containing 2% of potassium ferricyanide and 0.5% of sodium chloride, results in a slower growth, the form of the filaments is more irregular, and many larger structures are produced. In the stronger solution, growth usually ceases in about five minutes, whilst in the weaker solution it may continue for several hours. The action ceases when all the available potassium ferricyanide has been transformed, and may be renewed by adding more of the solution. The number of filaments may be limited by coating the metal with paraffin and removing the paraffin from very small areas before placing the metal in the solution. Experiments were made with iron, zinc, cobalt, cadmium, nickel, copper, lead, tin, chromium, and aluminium. For each metal which forms a precipitate with potassium ferricyanide there is a definite and characteristic type of precipitation structure. The presence or absence of a protective colloid has a marked influence on the kind of structure formed. Definite tubular filaments are produced from zinc, cadmium, and copper only in the presence of a protective colloid; in its absence, most of the precipitate appears "amorphous." Copper readily forms filaments in the absence of the protective colloid. The characters of structures produced with iron, zinc, cobalt, cadmium, copper, and nickel are described in detail. The form and rate of growth may be modified by the

passage of a weak electric current, by sudden changes in the concentration of the solution, and by the conditions of the surface of the metal, for example, whether rusty or not. All filaments are extremely sensitive to outside influences, such as jarring, causing currents, or addition of sand particles, any of which may cause change of direction of growth and change of form of filaments. Filaments grown on the surface show striking variations from those grown immersed. Certain metals, notably cadmium, show a rhythmic motion during growth. All these purely chemical and physical phenomena are significant in that they point the way to a better understanding of the phenomena of rhythm and periodicity in living beings.

CHEMICAL ABSTRACTS.

The Origin of Odour in the Molecules of Odoriferous Substances. HEINRICH TUDT (*Prometheus*, 1919, 30, 201—204, 209—211; from *Chem. Zentr.*, 1919, iii, 138—139).—The author assumes that the origin of odour must be within the molecule, since the odour of a chemical compound is not, in general, affected by external influences as long as the molecule remains undecomposed. The source can scarcely lie within the atom, since, if this were so, every odoriferous atom must retain its odour in the free state and in combination with odourless atoms; the monatomic elements are, however, odourless, as are the ions of the strongly odoriferous halogens. The cause of the odour is to be sought between the atoms in the molecule which contain the valency electrons. It must be assumed that odours are caused by the vibrations of valency electrons, since the molecules of odoriferous substances are not altered in any way by the emission of odour. It appears probable that the nasal sensory nerves have electron vibrations which are increased by resonance when odoriferous particles having corresponding intramolecular electron vibrations are drawn into the nose in admixture with air. The author's investigations are explained by numerous diagrams. He is led to the conclusion that a chemical element can the more readily induce odour in its compounds in proportion as its electrons are more firmly united to the atomic nucleus. Metallic atoms, in consequence of the ease with which they detach electrons, are not suited to the production of odour. It can readily be seen that in all the horizontal series of the periodic system the power of giving odour increases as the metallic character of the element diminishes from left to right; correspondingly, the stability of the union between the atomic nucleus and the respective electrons increases from left to right. The author explains, further, the odourless or odoriferous character of certain substances, such as methane, ethane, the higher paraffins, carbon tetrachloride, etc., as well as the spread of odour to a distance and other phenomena.

H. W.

Place and Mode of Origin of the Acetone Substances. ERNST KERTES (*Zeitsch. physiol. Chem.*, 1919, 106, 258—271).—Leucine was injected into the hind feet of dogs with an Eck's fistula and a "reverse" Eck's fistula. In the former case the injected sub-

stance is practically prevented from reaching the liver; in the second case, however, it does reach it. In the dogs with the "reverse" Eck's fistula, an increase in acetone, acetoacetic acid, and β -hydroxybutyric acid is recorded. The leucine does not alter the amount of excreted acetone substances in the dogs with Eck's fistula. The acetone substances, it is concluded, are therefore formed in the liver, and under certain physiological conditions they can be formed from leucine.

S. S. Z.

**Chemical Studies in Physiology and Pathology. VIII.
The Question as to Iodine Fixation in the Thyroid Gland.**

E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1919, **96**, 260—269. Compare A., 1918, i, 47, 241, 355, 357; this vol., i, 297).—The juices of pig's thyroid, human serum, and milk were treated with potassium iodide and $N/10$ -iodine, and then precipitated with hot 90% alcohol. A repeated extraction of the coagula with boiling water removed practically all the iodine which was retained. No iodine was removed in this way from untreated coagulated juice of thyroid. The amount of iodine extracted from the juice of thyroid by means of alcohol depended on the water content of the alcohol. The author considers that these experiments support the theory which he discusses, that iodine is a component part of the protein molecule of the thyroid gland, and that it is not an essential constituent of the thyroid secretion.

S. S. Z.

Alleged Irreciprocal Permeability of the Frog's Skin to Ions. MARTIN GILDEMEISTER and JUSSUF SCHÜKRI (*Biochem. Zeitsch.*, 1919, **96**, 241—248).—The authors cannot confirm the results obtained by Bayliss (A., 1908, ii, 712) that the skin of the frog conducts electric currents in Ringer's solution better from the outside to the inside than in the reverse direction. They therefore do not accept the conclusion arrived at by Bayliss that the skin of the frog is permeable to sodium ions from the outside, but not from the inside.

S. S. Z.

The Diazo-reaction of Normal Human Urine and the Influence of the Mode of Nutrition on the "Diazo Value."

OTTO FÜRTH (*Biochem. Zeitsch.*, 1919, **96**, 269—297).—The diazochromogen of normal human urine was investigated. Utilising his simplified method of isolating the hydroxyproteic acids from urine by decomposing the urea with soja urease, the author prepared a "baryta fraction" from the acid contents of the urine. The "baryta fraction" was further fractionated with various precipitating reagents before and after hydrolysis and the various fractions were studied. The conclusion arrived at is that diazochromogen, although not identical with histidine, is, however, a closely related iminazole derivative. Probably it consists of one or more transformation or condensation products of histidine produced by intermediate metabolism. Diazochromogen has further been found to be thermostable, soluble in alcohol, insoluble in ether, and separated only with difficulty by means of acetone from the alcoholic solution. It does not give Millon's reaction.

Another part of this investigation was devoted to the study of the "diao value" and the "diao quotient" of the urine of normal subjects, tubercular subjects in the early stage of the disease, underfed subjects who subsisted on a diet deficient in protein, and cachectic individuals. From these observations and those made by Masslow the author concludes that the iminazole complex contained in the diazochromogen is of endogenous origin.

S. S. Z.

Oxidation Procedure in the Human Organism. WALTER LASCH (*Biochem. Zeitsch.*, 1919, 97, 1—21).—As much as 12 grams per day of sodium thiosulphate can be consumed without harm. The thiosulphate is, however, not excreted as such in the urine, but is oxidised in the organism in accordance with the law observed by Tauber in the case of phenol. The ethereal sulphates increase slightly in the urine with intake of sodium thiosulphate. S. S. Z.

Origin and Significance of Acetoacetic Acid. L. C. MAILLARD (*Bull. Acad. med.*, 1919; from *J. Pharm. Chim.*, 1919, [vii], 20, 185—187).—A considerable quantity of acetoacetic acid was formed in a solution containing cycloglycylglycine, glycerol, and yeast-cells. The author suggests that the production of acetoacetic acid in the human body is due to the reduction of the dipeptide (removal of amino-groups), and not to an oxidising process. This conception appears to be more in harmony with the restricted oxidising faculty of diabetic subjects.

W. P. S.

Preparation and Physiological Action of some Derivatives of Meconic Acid. J. LAUTENSCHLAGER (*Biochem. Zeitsch.*, 1919, 96, 73—86).—The following derivatives of meconic acid were synthesised and tested for their physiological action. *Acetyl* derivative, $\text{OAc}\cdot\text{C}_3\text{HO}_2(\text{CO}_2\text{H})_2$, forms colourless needles, m. p. 218°. The *benzoyl* derivative crystallises in colourless leaves, m. p. 248° (decomp.). The *methyl hydrogen* ester forms colourless crystals, m. p. 161·5°; the *dimethyl* ester has m. p. 117°; the *propyl hydrogen*, *dipropyl*, and *diisobutyl* esters form colourless crystals, m. p. 165°, 105°, and 98° respectively; the *diamyl* ester is a colourless oil. The *urethane* derivative forms colourless crystals, m. p. 124°.

Meconylcarbamide, $\text{CO} \begin{array}{c} \text{C(OH):C} \quad \text{CO}\cdot\text{NH} \\ \diagdown \quad \diagup \\ \text{O} \\ \diagup \quad \diagdown \\ \text{CH}=\text{C} \quad \text{CO}\cdot\text{NH} \end{array} \text{CO}$, forms a yellow powder, m. p. 173° (decomp.), and its *ethyl*, *propyl*, and *allyl* ethers are white, crystalline powders, m. p. 138°, 141°, and 143° (all decomp.) respectively. *Meconylthiocarbamide* is a clear, yellow, crystalline powder, m. p. 181° (decomp.), and its *propyl ether* has m. p. 138° (decomp.).

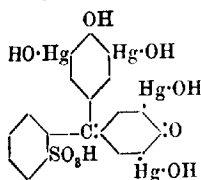
The acetyl and benzoyl derivatives and the aliphatic ethers of the acid produce, like the original acid, slight paralysis in the frog, but are inactive in the rabbit. The ethyl, and to a greater extent the propyl, ester produces a more marked action in the frog than the original acid. The corresponding monoalkyl derivatives are also

more active than the acid itself, but are not so potent as the normal esters. On the rabbit, however, this group of compounds produces no effect. The ether and diazo-compounds of the above esters behave physiologically like the esters themselves. The hydrazine derivative of meconic acid is very toxic and lethal in small doses.

The urethane derivative of meconic acid shows little potency, whilst the carbamide derivative is more active in the frog. The ethyl and propyl derivatives of the latter resemble meconic acid in their activity. Meconylthiocarbamide behaves like meconyl-carbamide, but is only one-third as potent. Its propyl derivative shows also some potency in the frog; in the rabbit the latter substances produce no effect. None of the synthesised substances has, therefore, manifested any definite narcotic action. S. S. Z.

Experimental Nephropathy produced by an Organo-mercury Compound of Phenolsulphonephthalein. J. EDWARD BURNS, E. C. WHITE, and J. G. CHEETAM (*J. Urol.*, 1919, **3**, 1—16).

—As phenolsulphonephthalein and mercury have special affinities for the secreting cells of the kidney it was thought that a compound containing these substances would attack these cells and not attack the other organs of the body, and the changes thereby produced would more nearly resemble the different types of nephritis found in the human being than those produced with other substances. The compound synthesised was tetrahydroxymercuriphenolsulphone-



phthalein, which probably has the annexed formula. It contains 63% of organically bound mercury. It is soluble in dilute alkali hydroxide. When given to dogs this substance produced acute and chronic renal lesions which resemble quite closely those found in the different types of nephritis in human beings. The lesions of the acute type were mainly tubular, although some slight glomerular changes were noticed. In the chronic type the most characteristic change is the increase of interstitial tissue both in the glomeruli and between the tubules, together with areas of tubular obliteration and glomerular fibrosis. Chemical examination of the blood and urine following the intravenous injection of sodium chloride and urea after the method of Underhill, Wells, and Goldschmidt (*J. Expt. Med.*, 1913, **28**, 322), showed results quite analogous to the type of lesion produced. This organo-mercury compound produced no lesions elsewhere in the body.

CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture

Comparative Studies on Respiration. VII. Respiration and Assimilation. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 2, 1—3).—Certain improvements in technique are described; thus when a reagent is employed which has a "buffer" effect it is desirable to have the same "buffer" action during the measurement of normal respiration as during exposure to the reagent. An indicator should be present in the liquid containing the organisms, so that changes in reaction may be observed. Preliminary results indicate that there is pronounced antagonism between such substances as sodium chloride and calcium chloride in their effect on respiration.

J. C. D.

Comparative Studies on Respiration. VIII. The Respiration of *Bacillus subtilis* in Relation to Antagonism. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1919, 2, 5—15).—In relatively low concentrations of sodium, potassium, and calcium chloride the rate of respiration of *B. subtilis* remains fairly constant for a period of several hours, whilst in higher concentrations there is a gradual decrease in the rate. The effects of salts on respiration show a well-marked antagonism between sodium chloride and calcium chloride and between potassium chloride and calcium chloride. The antagonism between sodium and potassium chlorides is slight.

J. C. D.

Comparative Studies on Respiration. IX. The Effects of Antagonistic Salts on the Respiration of *Aspergillus niger*. F. G. GUSTAFSON (*J. Gen. Physiol.*, 1919, 2, 17—24).—In relatively dilute solutions sodium chloride and calcium chloride increase the respiration of *Aspergillus* in the presence of dextrose. Higher concentrations cause a decrease, probably due to the osmotic effects of the salts. The antagonism between sodium chloride and calcium chloride could be demonstrated by a study of the respiration of this organism. Spores germinated on a medium containing 0.5*M*-sodium chloride and 0.05% of dextrose, but failed to do so when calcium chloride was used instead of sodium chloride, or when both salts were present. Apparently a substance may have different effects on respiration from those which it has on growth. J. C. D.

Proteinogenous Amines. IV. The Production of Histamine from Histidine by *Bacillus coli communis*. KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, 39, 539—584).—*Bacillus coli communis* does not form histamine from histidine when acting alone, in the presence of nitrates or ammonium salts, or in a medium containing glycerol. When glycerol or dextrose and a source of nitrogen, such as potassium nitrate or ammonium chloride, are present, some 50% of the histidine is con-

verted into histamine. Under these conditions the medium become acid, and the suggestion is advanced that histamine is produced by the bacillus as a means of neutralising the acid produced from glycerol. Contrary to many statements, it is found that histamine is never produced except in the presence of an easily available source of carbon.

J. C. D.

Formation of d - β -Iminazolyl-lactic Acid from l -Histidine by Bacteria. K. HIRAI (*Act. Schol. Med. Kyoto*, 1919, 3, 49—53; from *Physiol. Abstr.*, 1919, 4, 256).—Histidine hydrochloride, prepared from ox blood, was acted on for forty days in protein-free nutrient media with a strain of *Proteus vulgaris* which was capable of converting l -tyrosine into γ -hydroxyphenyl-lactic acid. The product was separated by precipitation with phosphotungstic acid; it crystallised with $1H_2O$ and had $[\alpha]_D^{25} + 33.7^\circ$, the yield being 11%. It was identified by elementary analysis and by means of the platinichloride.

H. W.

Application of the Fixation Method in Bacterial Fermentation. I. Acetaldehyde as an Intermediate Product in the Fermentation of Sugar, Mannitol, and Glycerol by *Bacillus coli*, Dysentery, and Gas Gangrene Organisms. C. NEUBERG and F. F. NORD (*Biochem. Zeitsch.*, 1919, 96, 133—158).—By employing sodium sulphite and calcium sulphite as "fixing" agents, acetaldehyde has been established as an intermediate product in the fermentation of dextrose, mannitol, and glycerol. *B. coli* was employed in the fermentation of dextrose, Flexner Y and Shiga-Kruse cultures in the fermentation of mannitol and Fränkel's bacillus (*B. Welchii*) in the fermentation of glycerol. As the last-mentioned organism is an anaerobe the possibility of the formation of acetaldehyde as a secondary product from the alcohol produced is excluded.

S. S. Z.

Application of the Fixation Method in Bacterial Fermentation. II. The Establishment of an Aldehyde Stage in Acetic Acid Fermentation. C. NEUBERG and F. F. NORD (*Biochem. Zeitsch.*, 1919, 96, 158—175).—Alcohol was fermented in the presence of calcium sulphite with *Bacterium Orléanense*, *B. Ascendens*, and *B. Pasteurianum*. In each case acetaldehyde was established as an intermediate product in the fermentation.

S. S. Z.

Acid Fermentation of Xylose. E. B. FRED, W. H. PETERSON and AUDREY DAVENPORT (*J. Biol. Chem.*, 1919, 39, 347—383).—Xylose is readily fermented by bacteria which are found in fresh silage, sauerkraut, and manure, and also in certain soils, but the organisms commonly studied in the laboratory failed to break down the sugar. The organisms which can effect the fermentation are readily isolated in pure culture. The fermentation takes place either in the presence of free oxygen or in a limited supply, and the main products formed are acetic acid and lactic acid. The

relation of acetic acid to lactic acid approaches the theoretical ratio of 40 to 60 that would obtain if these two compounds were the only products arising from fission of the xylose molecule. Traces of carbon dioxide and ethyl alcohol were detected. Other sugars are fermented by these xylose-fermenting bacteria. J. C. D.

Mode of Action of Metal Sols. C. R. MARSHALL (*Proc. Roy. Soc. Edin.*, 1918-19, **39**, 143-148).—An attempt to ascertain how silver in a particular form, such as colloidal silver solutions (Bredig), can exert a bactericidal action. The impact of the larger submicroscopic particle is not the cause, whilst there is no evidence that adsorption of the silver particle takes place on the surface of the organisms. Electropositive and electronegative sols produced the same antiseptic action. The concentration of free silver ions was insufficient to explain the pharmacological action, but when the size of the particles was considered it was found that the bactericidal value may be ascribed to the ultra-microscopic particle below $13\ \mu$ in diameter. J. C. D.

Vitamine Requirements of certain Yeasts. FREDA M. BACHMANN (*J. Biol. Chem.*, 1919, **39**, 235-257).—The observations of Pasteur and of Wildier on the nutritive requirements of yeast are confirmed. All the yeasts investigated grew better and fermented more readily in a medium containing some small amounts of organic material other than sugar. It is suggested that the substances which are necessary for fermentation to be carried out effectively by the yeast are of the nature of vitamins (Wildier's "bios," *La Cellule*, 1901, **18**, 313). The yeasts appear to vary considerably in their requirements for this accelerating factor. J. C. D.

Action of Radium Emanation on the Vitamines of Yeast. KANEMATSU SUGIURA and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1919, **39**, 421-433).—This investigation showed that exposure to radium emanation may cause partial destruction of the vitamins present in yeast. It is suggested that a part of the beneficial influence of radium in the treatment of malignant tumours may be dependent upon such destruction of the growth-accelerating factors. J. C. D.

The Metabolin and Antibolin of Yeast. E. VAHLEN (*Zeitsch. physiol. Chem.*, 1919, **106**, 133-178).—The author has prepared metabolin and antibolin from yeast which, although not quite identical with the similar principles previously extracted by him from the pancreas of cattle, resembled them in their main properties. Metabolin accelerates alcoholic fermentation, antibolin has the opposite effect. The principles can be transformed into each other by molecular rearrangement. An irreversible metabolin has also been prepared from yeast and potatoes. This metabolin also accelerated alcoholic fermentation and reduced the amount of sugar in the urine of diabetic patients on two occasions. S. S. Z.

The Content and the Formation of Invertase in Yeast. H. VON EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1919, **106**, 201—249).—The inversion capacity of two strains of yeast examined from time to time has been proved to be constant. The optimum temperature for invertase formation in one of these strains has been found to be 26—30°. When the temperature was raised by about 35° no invertase formation could be observed. The invertase formation is further dependent on the acidity of the medium. The maximum enzyme formation coincides with the optimum activity of the invertase. At a H-ion concentration higher than $P'_H=2$ the invertase is destroyed; on the other hand, at a H-ion concentration of $P'_H=6-7$ the enzyme formation is 90% of its optimum. Water at a temperature of 10° does not wash out the invertase of fresh living yeast. S. S. Z.

The Augmentation of the Catalase Activity of Yeasts. HANS VON EULER and INGVAR LAURIN (*Zeitsch. physiol. Chem.*, 1919, **106**, 312—317).—The catalase of *Saccharomyces Thermantitonus* is activated by chloroform, but not by an increase of temperature. Sunlight diminishes the action of catalase in living yeast cells, whilst X-rays have no effect on it. S. S. Z.

Ilex vomitoria as a Native Source of Caffeine. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1919, **41**, 1307—1312).—Since the so-called "Paraguay Tea," which contains considerable proportions of caffeine, is derived from certain South American species of *Ilex*, the authors have examined other representatives of this genus found in the south-eastern States in order to discover possible home sources of the drug. Several species were found to contain no caffeine at all, but *Ilex vomitoria*, Aiton, appears to be worth cultivating as a source of the base. Under the name "Yaupon," the leaves were already used by the Indians for their medicinal and stimulating properties. J. C. W.

Action of Cyanamide and of Dicyanodiamide on the Development of Maize. P. MAZÉ, VILA, and M. LEMOIGNE (*Compt. rend.*, 1919, **169**, 804—807).—The results of water-culture experiments show that cyanamide at a concentration of 0.162 gram per litre prevents the germination of maize seeds, but that dicyanodiamide at this concentration is not toxic towards their germination.

Similarly, cyanamide, either with or without the presence of sodium nitrate, kills maize seedlings, whereas dicyanodiamide, in the presence of sodium nitrate, does not appreciably check the development of the plant, although with dicyanodiamide as the only source of nitrogen, the plant does not increase in weight, but yet remains alive for several months. W. G.

Presence of Formic Acid in the Stinging Hairs of the Nettle. LEONARD DOBBIN (*Proc. Roy. Soc. Edin.*, 1918-19, **39**, 137—142).—Although it is frequently stated that formic acid is present in the stinging hairs of the nettle, few attempts at a direct

proof have been made. The author collected the acid present in a very large number of hairs by compressing the leaves with filter-paper impregnated with barium carbonate. From an examination of the barium salt formed he comes to the conclusion that free formic acid does exist in the stinging hairs. J. C. D.

The Yellow Colouring Substances of Ragweed Pollen.

FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1919, **41**, 1285—1289).

—The pigments of ragweed pollen may be extracted by alcohol, then precipitated in fractions from an aqueous solution by means of basic lead acetate, and finally recovered from the lead precipitates in the usual way, the yield being about 0.6%. The least soluble pigment is a quercitrin glucoside, $C_{27}H_{30}O_{12}$, which fuses at 228—229° to a cherry-red oil, and thus differs from its three known isomorphs, quercimeritrin, isoquercitrin, and incarnatin. Among the more soluble glucosides is one which yields isorhamnetin on hydrolysis, and this seems to be predominant. J. C. W.

Soil-sorption.

E. RAMANN and A. SPENGLER (*Landw. Versuchs-Stat.*, 1918, **92**, 127—146).—The interchange of bases occurring in mixed solutions containing two different bases has been studied by means of a permutite of moderately constant composition prepared in the wet way. The replacement of bases taking place when such a hydrated aluminium alkali silicate is treated with neutral potassium, ammonium, calcium, and sodium salts has the character of a chemical exchange, no signs of physical adsorption being detectable. The interchanges are by equivalents, that of potassium and ammonium following the law of mass action; the curves expressing the ratios of the ions in solution and those of the bases in the silicates are coincident. In solutions containing sodium and calcium salts the interchange of bases corresponds predominantly with the ratio of the ions in the solution, but preponderance of the calcium or sodium salts results in divergences dependent on a second factor of unknown nature. Potassium and ammonium are mutually replaceable, and displace sodium and calcium completely from the silicate, whereas the displacement of potassium and ammonium by sodium and calcium is incomplete. The ratios between the bases in the solutions and in the silicates have different values. Bases present in small proportions in the solutions are combined by the silicate in amounts greater than those corresponding with such proportions. Within wide limits, the absolute concentrations of the salts in the solution are without appreciable influence on the composition of the silicate, this being the case even with mixtures of calcium salts with those of the univalent metals. T. H. P.

Solubility of Calcium Carbonate of Different Origins and Degrees of Fineness in Water containing Carbon Dioxide in Relation to Soil and Plants. G. HAGER and J. KERN (*J. Landw.*, 1916, **64**, 325—342).—The degree of fineness of calcium carbonate influences considerably its solubility and especially its velocity of dissolution in water containing carbon dioxide.

The less prolonged the action and the greater the proportion of carbon dioxide in the water, the more marked are the differences observed with carbonates of different finenesses. The increased rapidity of dissolution, as well as the more effective distribution obtainable, probably causes the superior action on soil and plants of the more finely ground carbonate.

T. H. P.

Determination of the Efficacy of the Soil Feeding Stuff, Phosphoric Acid and Potash, by Culture Experiments, and Determination of their Relative Solubility by Acids. O. LEMMERMANN, A. EINECKE, and L. FRESSENIUS (*Landw. Versuchs-Stat.*, 1916, **89**, 81—195).—A large number of pot experiments have been carried out with soils of different types, analyses of the soils especially as regards the relative solubilities of the phosphates and potassium compounds being also made. Determinations of such solubilities furnish in most cases a means of expressing the physiological efficiency of these fertilising substances. In the case of the phosphates, the best of the various solvents tried for determining the relative solubility proves to be 1% citric acid solution, and the soil may be extracted by dropping the solvent through it or by shaking it with the solvent. For potash, on the other hand, this solvent is too weak, and satisfactory results have been obtained by the use of 10% hydrochloric acid. In these determinations allowance must be made for the physical characters of the soil. The common assumption that the potassium compounds of the better soils are more difficultly soluble than those of the lighter ones is not supported by the results obtained; such assumption applies more in the case of the phosphates, this being perhaps attributable to the higher clay- and iron-contents of the better soils. The degree to which plants are able to utilise the phosphoric acid appears to increase with the poverty of the soil in phosphates.

T. H. P.

Comparison of Two Fertilisers according to Mitscherlich's Law of the Minimum. MARYAN GORSKI (*Landw. Versuchs-Stat.*, 1919, **93**, 113—120).—Results obtained in fertilising experiments with increasing proportions of ammonium sulphate and sodium nitrate agree well with Mitscherlich's mathematical expression (A., 1911, ii, 760). It is shown that equality of the efficiency factors (*Wirkungsfaktoren*) for corn- and straw-yields necessitates constancy of the ratio, corn-yield:straw-yield, for different minimum factors. Calculation of the ratio between the efficiency factors for ammonium sulphate and sodium nitrate gives values which remain almost unchanged, no matter whether the efficiency factors of the corn-yield or those of the straw-yield are employed in the calculation.

T. H. P.

General and Physical Chemistry.

Eykman's Refractometric Investigations in Connexion with the Presentation of the Edition of His Works. A. F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1200—1203).—A short account of Eykman's unpublished work on the refractometric measurements of organic compounds given on the occasion of the publication of a collection of his published and unpublished work.
J. F. S.

Molecular Refractivity of Cinnamic Acid Derivatives. ERIC WALKER and THOMAS CAMPBELL JAMES (*T.*, 1919, **115**, 1243—1247).

The Line Spectrum of Sodium as Excited by Fluorescence. R. J. STRUTT (*Proc. Roy. Soc.*, 1919, [A], **96**, 272—286).—Bakerian Lecture. An improved sodium vapour lamp is described. This consists of a dumbbell-shaped quartz tube placed vertically. In the lower bulb is a pool of sodium which constitutes the cathode. Electric connexion is made by means of an iron or copper wire. The anode consists of a tungsten rod. The lamp is evacuated by means of a Gaede pump. A concentric ring burner surrounds the base of the cathode bulb, by means of which the sodium is kept at a temperature of 180°. The lamp can be run for short periods by a current of 5—6 amps. on a 200 volt circuit, but for prolonged working a lower current, 2.5 amps., is preferable. The lamp is started by means of an induction coil, the terminals of which are connected to the cathode and the constriction of the lamp tube. Using the light from this lamp, the author has examined the resonance effects of sodium vapour. It is shown that excitation of sodium vapour by the second line of the principal series leads to emission of both 3303 and the *D* lines, and that excitation of the *D* lines leads to the emission of the *D* lines only, with 3303. When *D* light falls on sodium vapour of appropriate density, it is known that an intense surface emission occurs from the front layer, and a weak one from succeeding layers. Analysis by absorption in an independent layer of sodium vapour shows that the superficial emission is more absorbable, and therefore nearer the centre of the *D* lines. The breadth of the *D* lines in superficial resonance has been estimated by interferometer methods. It is found to correspond with the breadth conditioned by the Doppler effect, on the assumption that the luminous centre is the sodium atom. Polarisation could not be detected in the ultra-violet radiation, although in accordance with previous observers it was readily observed in *D* resonance.
J. F. S.

The Ultimate Rays in the Arc Spectra of the Elements. M. A. CATALÁN (*Anal. Fis. Quim.*, 1917, 15, 487—498, and 1918, 16, 513—519).—A criticism of the conclusions of Gramont (A., 1907, ii, 517, and A., 1908, ii, 645) regarding the ultimate rays of a spectrum. Contradicting the assertion of Gramont, the author shows that in general the ultimate rays in the arc spectra are those of the greatest intensity. This conclusion is supported by a special study of the arc- and spark-spectra of columbium, zirconium, and titanium. W. S. M.

The Logarithmic Law connecting Atomic Number and Frequency Differences in Spectral Series. GLADYS A. ANSLOW (*Physical Rev.*, 1919, 13, 326—336).—Straight lines are obtained by plotting the logarithms of the atomic numbers against the logarithms of the constant frequency differences occurring in the spectral lines of most of the alternate members of Groups I, II, and III of the periodic table; also for sulphur and selenium. Two systems of four approximately straight lines approaching parallelism result when the family has both doublet and triplet series. Equations derived are of the form $\nu = (N/mnk)^{-1}$, where N is the atomic number, A is a constant depending on the system, n is an integer which is the same for both families in any group, k is a constant, 0.080, and m acquires successive integral values for the ν , $\nu_1 + \nu_2$ and ν_1 equations. Elements of high atomic number should lie above the family line. These results indicate the need of modifying the Bohr-Sommerfeld theory of atomic structure before using it for predicting optical series. CHEMICAL ABSTRACTS.

The Constitution of the Atom and the Properties of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1919, 169, 745—752).—A continuation of the theoretical discussion of this subject (compare this vol., ii, 206, 310, 441) and its application to the band spectra of carbon, nitrogen, and cyanogen. The following explanation of the known facts is given. The nucleus of the atom is a cylinder with circular base, which rotates round its axis, its thickness in the direction of the axis being the same for all atoms, but the diameter of the circular base being variable. The nucleus is the seat of longitudinal vibrations developed in the direction of the axis. The thickness being constant, the fundamental vibration is the same for all the elements, the higher harmonics giving the frequencies of the band maxima in the successive spectra. On the main longitudinal vibration are superposed the vibrations of the rings of electrons in three directions in space. The divisions imposed on the nucleus by the nodal surfaces may explain the variations of the elementary groups and their simplification with increasing frequency.

These vibrations require that the shocks in the direction of the axis are propagated with a velocity notably inferior to that of light. The special substance of the nucleus is supposed to be electrified in its mass, and can be likened to ordinary matter rather than to a vacuum, for the propagation of small displacements. W. G.

Study of the Stability of some Solutions of Enzymes and Alkaloids by means of Ultraviolet Absorption Spectra. The Particular Cases of Pancreatin and Morphine.

DAMIANOVICH and ADOLFO WILLIAMS (*Anales Soc. Cient. Argentina*, 1917, **84**, 79—91).—In order to determine the degree of absorption, Dhéré's method was used ("Spectrographic Researches on the Absorption of Ultraviolet Rays by Albuminoids, Proteins, and their Derivatives," Univ. of Fribourg, 1909). Aqueous alkaline solutions of pancreatin yielded spectra indicating a gradual absorption in the extreme ultraviolet, but without any band indicating selective absorption. Compared with Dhéré's results a notable difference was observed. Albuminoid substances show an absorption band in the ultraviolet spectrum which for a given concentration and thickness includes radiations between 2927 Å. and 2628 Å., whereas in the given case the band did not appear in a solution of 10:1000 strength and 5–10 mm. thickness. Solutions were submitted to temperatures between 40° and 110° for one-half to forty-eight hours. Some alteration in the absorption was noticeable; the conclusion was reached that temperature influences the action. Substances such as glycerol, peptone, and casein, which protect trypsin or pancreatin against the destructive action of heat, act in a similar way towards causing a variation in the ultraviolet spectrum. A solution of morphine (1:10,000) showed appreciable absorption in the ultraviolet, as did also solutions of theobromine, but no band was observed, although neutral aqueous solutions of the hydrochloride showed a faint band between 2950 Å. and 2767 Å. The addition of sodium carbonate (3% solution) to a solution of morphine hydrochloride (1:1000) produced absorption of the extreme ultraviolet and a clear absorption band which increased somewhat with the temperature. Sodium hydroxide causes a similar displacement.

CHEMICAL ABSTRACTS.

Observations and Measurements on Optically Active Crystals (NaClO₃).

ELIGIO PERUCCA (*Nuovo Cim.*, 1919, [vi], **18**, ii, 112—154).—The author describes a new polarimetric arrangement, which he has applied to the measurement of the rotatory power of pure, crystalline sodium chlorate and of crystals of the chlorate coloured with "extra China blue" [probably sodium (or ammonium) triphenyltri-*p*-aminodiphenyltolylcarbinoldi-(or mono-)sulphonate], which exhibits a very sharp absorption band in the green. These coloured crystals are obtained, although not always, by moderately rapid cooling of a hot saturated solution of the chlorate and the colouring matter; ultramicroscopic examination of the crystals shows that the blue dye is not present in them in the colloidal condition.

The results obtained indicate that only as a first approximation can the rotatory power of solid sodium chlorate be regarded as a constant, variations greater than the experimental error being observed with different crystals and also with one and the same crystal in different directions and at different points. The mean value obtained for $[\alpha]_D^{20}$ is +3.120°. The rotational dispersion,

which shows no deviations from the curve of normal dispersion greater than the errors of observation, may be expressed for the temperature 13° by the following equation, λ being in $\mu\mu$ and $[\alpha]_\lambda$ in degrees: $[\alpha]_\lambda = 1168300/\lambda^2 - 0.3514 + 0.000000306\lambda^2$; Lowry's formula, $[\alpha]_\lambda = a/(\lambda^2 - b)$ (T., 1913, **103**, 1067) is inapplicable in this case.

With the coloured crystals, for the light comprised in the spectral zone absorbed (maximal absorption at about $\lambda = 548\ \mu\mu$), the rotatory power is found to vary when the crystal is rotated round the light ray as axis, that is, to vary with the azimuth of the crystal with respect to the incident luminous vibration. The course of this variation is sinoidal, and for $\lambda = 546.1$ the maximum variation amounts to as much as 1° per 3.66° for a thickness of 1 millimetre. With crystals deeply coloured, more marked effects still are observed; thus, in one case, for $\lambda = 589.3\ \mu\mu$, the difference between the maximal and minimal rotations per millimetre of thickness reached 1.3° . In no instance, however, was change in the sign of the rotation found. There appears to be no very simple relation between the intensity of the coloration and the extent of the variation in rotation. This phenomenon persists without marked alteration when the crystals are heated to about 85° , but at this temperature it suddenly disappears and does not reappear when the crystals are cooled.

In these artificially coloured sodium chlorate crystals there is, as a rule, co-existence of two tetrahedra, each of which, united to a pentagonal dodecahedron, is characteristic of crystals having rotatory power of a certain sign and of normal magnitude at all points. Groth (*Ann. Phys. Chem.*, 1876, **158**, 214) refers to the possibility of the co-existence of two tetrahedra in a single crystal of sodium chlorate, but the author was unable to obtain such a crystal under widely varying conditions of crystallisation.

T. H. P.

Precision Measurements in the X-Ray Spectra. II. The X-Ray Spectrum of Tungsten. MANNE SIEGBADN (*Phil. Mag.*, 1919, [vi], **38**, 639—646. Compare this vol., ii, 261).—The *K* and *L* series of X-ray lines have been measured for tungsten by means of a spectrograph built on the same principle as that previously described (*loc. cit.*). The measurements were made with rock-salt ($\log 2d = 0.7503541$) and calcite ($\log 2d = 0.7823347$), and the two sets of results shown to be remarkably close to one another, a fact which speaks for the accuracy of the calcite lattice constant in reference to that of rock-salt. In the *K* series the strongest line, $K\alpha$, has the value 208.85XU , the α_2 line is determined with reference to the α_1 line and the value $K\alpha_2 = 213.52\text{XU}$ obtained. The lines $K\beta_1$ and $K\beta_2$ have the values 184.36 and 179.40 respectively. The values are compared with those of de Broglie, Hull and Rice, Dauvillier, and Dershem, and those of the last-named shown to be most nearly in accord with the author's work. The measurement of the *L* series was carried out with the vacuum spectrograph previously described (*loc. cit.*). The following values were obtained: $L\alpha_1$, 1473.48 ; $L\alpha_2$, 1484.52 ; $L\beta_1$, 1279.17 ; $L\beta_2$, 1241.91 ; and $L\gamma$

1095.53. The fainter lines of this series have been measured with reference to one of the stronger lines, and the following frequency differences obtained: $\epsilon - \eta = l - \eta = 98.76$; $\beta - \alpha' = \beta_1 - \alpha_2 = 98.54$; $\delta - \gamma = \gamma_1 - \beta_2 = 98.05$; $\theta - \zeta = \gamma_2 - \beta_3 = 97.55$. These figures confirm to a certain extent Sommerfeld's view that the L series can be divided into two groups with constant frequency differences between the lines.

J. F. S.

Precision Measurements in X-Ray Spectra. III. An X-Ray Spectrograph for Medium Wave-lengths. MANNE SIEGBAHN and A. B. LEIDE (*Phil. Mag.*, 1919, [vi], **38**, 647—651. Compare preceding abstract).—An X-ray spectrograph is described which is designed to bridge the regions measured by the instruments described in the previous papers (*loc. cit.*). In the present instrument the slit is placed behind the crystal. The crystal table is in fixed connexion with a high precision circle scale which can be turned in relation to the slit and plate-holder. To fix the crystal in the required position and for micrometrical adjustments, the circle is provided with a tangent screw attached to the arm for the plate-holder. Crystal table and plate-holder as a whole can be turned about the same axis. A circle scale and nonius on the back of the spectrograph serve to give an approximate adjustment of the crystal to receive the X-ray pencil under the reflexion angle required. The plate-holder and slit stand are mounted on the same bed-plate, and a thick lead cover is laid over to prevent blackening through diffused rays. Calcite crystals alone have been used with this instrument. The measurement of the reflexion angle is carried out as follows. A fine slit (with gold edges) is adjusted, so that the normal from the rotating axis to the photographic plate passes through it. The crystal is placed on the table with its reflecting plane in the rotation axis. The crystal is then turned so that the normal slit-plate forms an angle with the crystal face approximately equal to the reflexion angle for the spectral line sought. This is done in two ways; in one case the plate-holder may be turned to the right side in order that the incoming pencil shall be reflected; in the other case a turning of the plate-holder to the left is necessary. This spectrograph is suitable for wave-lengths 0.5 Å.U. to 20 Å.U. The instrument has been tested on measurements of $\text{CuK}\alpha$. In a previous paper, using the vacuum spectrograph, the value $\lambda = 1537.36 \text{ Å.U.}$ was obtained; with the present instrument the value $\lambda = 1537.44 \text{ Å.U.}$ is found; the difference 0.005% is attributed to a lack of information of the temperature-coefficient of the lattice constant of calcite.

J. F. S.

The Radioactivity of the Water from the Principal Spring at Bagnoles-de-l'Orne and its Variations. P. LOISEL (*Compt. rend.*, 1919, **169**, 791, 792). The water of Bagnoles contains from 22×10^{-12} to 109×10^{-12} grams of dissolved radium per litre, the mean value being 68×10^{-12} grams per litre. The amount of radium emanation in solution varies from 0.0002–0.0015 micro-curie per litre.

W. G

Application of the Thermionic Amplifier to Conductivity Measurements. R. E. HALL and L. H. ADAMS (*J. Amer. Chem. Soc.*, 1919, **41**, 1515—1525).—The use of an amplifier in conjunction with the telephone in the measurement of the resistance of solutions makes the determination of the point of balance on the bridge much simpler. Any ordinary telephone becomes a much more sensitive instrument with an amplifier than the best telephone without it. When a sensitive telephone is used, the current through the bridge may be reduced to a tenth of the value necessary without the amplifier, and the instrument will still have several times the sensitiveness it has without the amplifier. An electron tube may be used as a source of alternating current for conductivity measurements. Its advantages are its cheapness and the wide range of frequencies which may be obtained with it. A first harmonic is present in the current, which is noticeable at low frequencies, but which is not troublesome at a frequency of 1000 cycles or more. If, for any reason, it should be desired to use frequencies in conductivity measurements beyond the limit of the human ear, a telephone could still be employed to indicate the bridge balance by the use of the autodyne method. J. F. S.

Preparation of Conductivity Water. C. B. CLEVINGER (*J. Ind. Eng. Chem.*, 1919, **11**, 964—966).—The apparatus described is a modification of the Bourdillon still (*T.*, 1913, **103**, 791); the steam, obtained from water containing phosphoric acid or potassium hydrogen sulphate, is led through a coil and trap, and then enters a vertical tin tube about 6 feet long, the inlet for the steam being at about the middle of the vertical tube. The latter is fitted with condensing jackets, one at the top and the other near the lower end, which is bent into the form of a trap and enters the containing vessel for the conductivity water. A current of pure air is admitted to the vertical tube through a side-tube just below the lower condensing jacket; this current of air ascends the vertical tube, mixes with the steam, and carries off any remaining impurities through the upper end of the tube. The various parts of the apparatus are made of tin-coated metal, and the upper end of the vertical tube is connected with absorption vessels for preventing the entrance of ammonia, etc. [See, further, *J. Soc. Chem. Ind.*, 1919, 928A.] W. P. S.

Behaviour of Electrolytic Ions in Solid Substances. Conductivity of Permutite Mixtures. A. GUNTHER-SCHULZ (*Zeitsch. Elektrochem.*, 1919, **25**, 330—333).—The specific resistance and temperature-coefficient of twenty-one pure permutites have been determined by the method previously described (*A.*, 1915, ii, 149). It is shown that in their preparation, in addition to an interchange of base, some permutites adsorb considerable amounts of salts. The specific conductivity of potassium-silver permutite and sodium-silver permutite of a series of compositions has been measured, and it is shown that in the former case the conductivity can be calculated according to the simple mixture

rule, whilst in the latter case this is only approximately true. On the assumption that the law of reciprocal influence of two salts with a common ion on the degree of ionisation holds, it follows that sodium, potassium, and silver permittite are dissociated to approximately the same extent.

J. F. S.

Is the Electrical Conductivity of the Elements Conditioned by the Presence of Isotopes? F. H. LORING (*Chem. News*, 1919, 119, 199—200. Compare this vol., ii, 384).—A theoretical paper in which various points dealt with in the previous paper (*loc. cit.*) are discussed in the light of the publications of other investigators.

J. F. S.

Anodic Polarisation. II. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 1349—1351).—An explanation of the phenomenon previously described (*ibid.*, 1918, 20, 1121) is given. Iron can only exist in a state of internal equilibrium in a solution which contains no ferric ions. The presence of ferric ions disturbs the equilibrium, the more the greater the concentration of the ferric ions. The potential of iron is therefore less negative in a solution that contains ferric ions than in one which is free from ferric ions. In the solution with which the stated phenomenon was obtained, the iron consequently did not present the potential of internal equilibrium, but a less negative potential. In such a liquid, iron, when brought into solution, will change the concentration of the electrolyte in the neighbourhood of the electrode. The iron goes into solution exclusively as ferrous ion. During this anodic solution, the internal equilibrium is disturbed, as is indicated by the less negative potential, and, at the same time, the metal is surrounded by a liquid layer poorer in ferric iron than the rest of the solution. After the current has been broken, the iron approaches internal equilibrium with great rapidity, and on account of the decrease in ferric-ion concentration in its immediate neighbourhood, will exhibit a more negative potential than before polarisation. This state can, however, only persist for a short period, since the ferric ions diffuse from the outside into the boundary layer, and so the potential becomes less negative, and eventually reaches its initial value.

J. F. S.

Electrical Characteristics of Pigment Colloids. RUDOLF KELLER (*Kolloid Zeitsch.*, 1919, 25, 60—62).—In works of reference on colloids, among others in that of Zsigmondy, it is stated that basic colour substances in colloidal solution travel towards the cathode, acid substances towards the anode, under the influence of an electric current. The author finds that this is not a general rule, for alkaline solutions of methylene-blue and acid magenta travel to the anode and acid solutions of the same substances travel to the cathode. The reason for this behaviour is probably that in the first place pigment colloids, which have neither strong acidic nor strong basic characteristics, obtain their electric charges, according to Cohen's rule, by virtue of the ratio of the dielectric

constant compared with that of water, and in the second place from the electric charges of the dispersion medium. J. F. S.

Table of P_H , H' and OH' Values corresponding with Electromotive Forces determined in Hydrogen Electrode Measurements, with a Bibliography. CARL L. A. SCHMIDT and D. R. HOAGLAND (*Univ. California Pub. Physiol.*, 1919, 2, 23—69).—The table includes values of P_H from 0.034 to 14.032. The bibliography of 467 titles covers the entire field of hydrogen-ion concentration up to 1919. The methods for the determination of hydrogen-ion concentration are reviewed.

CHEMICAL ABSTRACTS.

Discharge Electrolysis. Electrical Colloid Syntheses. V. KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1919, 25, 309—323).—An electrical method for preparing colloidal metals is described which consists in electrolysing water with either direct or alternating current combined with a condenser circuit. The author terms the process "discharge electrolysis." Experiments are described in which colloidal copper is produced by the electrolysis of ordinary distilled water by means of direct current (96 volts) or alternating current (125/8000 volts), using two copper electrodes close together with a condenser in a parallel circuit. It is shown that when a discharge of at least 100 volts passes between two copper electrodes in distilled water, the cathode is disintegrated into fairly large particles, but if an oscillating parallel circuit is combined with the main circuit, the disintegration passes over, more or less completely, according to conditions, to the anode, and colloidal copper oxide is produced. Experiments with direct current show that an increasing capacity in the secondary circuit and a decreasing resistance in the main circuit increase the amount of disintegration, but, at the same time, the characteristic action of the oscillating circuit becomes more and more predominating. The disintegrated metal and the colloidal oxide are easily separated. The nature of the colloidal oxide depends on which of the two circuits predominates in its formation. The smaller the current strength and the capacity, the smaller are the colloidal oxide particles. The effect is produced because the electrolytic current covers the anode with a disperse oxide layer, and this is disintegrated by the spark discharge. When alternating current is used, the process is helped by a depolarising action of the cathodic component. J. F. S.

Auto-complexes in Solutions of Cupric Chloride and Cupric Bromide. STEWART BYRON WATKINS and HENRY GEORGE DENHAM (*T.*, 1919, 115, 1269—1279).

Magneto-chemistry of Chromous and Oxychromic Salts. B. CABRERA and S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1919, 17, 149—167).—An account of a series of measurements of the magnetic susceptibility of solutions of chromous salts. The apparatus and the method of Quincke were employed. For the chromous

ion in sulphate and chloride solutions, the integral number 24 was obtained for the number of magnetons. The oxychromic salts of the formulæ $\text{Cr}_2\text{O}(\text{SO}_4)_2$ and Cr_2OCl_4 , each in the violet and the green modification, were also studied. Integral numbers of magnetons for these complex cations were not obtained.

W. S. M.

Maximum Temperature [Limit]. WALTHER JANKOWSKY (*Zeitsch. Elektrochem.*, 1919, 25, 325—328).—A theoretical paper in which, from a consideration of heat of reaction at medium temperatures, it is shown that this quantity is developed for the most part by a conversion of potential energy into heat. From this deduction, it follows that not only must an absolute zero of temperature exist, but that there must also be an absolute upper limit (maximum temperature). The absolute zero is defined as that temperature at which the energy content of a substance consists entirely of potential energy and at which a conversion of potential energy into heat is impossible. The maximum temperature is defined as that temperature at which the energy content consists entirely of heat and at which the conversion of heat into potential energy is impossible. All heat changes, inclusive of chemical reactions, must occur between these two temperature limits. In the neighbourhood of both points, the thermal properties of all substances approach the zero value. Both temperature limits are only reached asymptotically.

J. F. S.

Investigation of Mewes' Law of the Relation between the Volume of a Gas and the Temperature. RUDOLF MEWES and

LEO WIG NEUMANN (*Zeitsch. Sauerstoff. Stickstoff. Ind.*, 1919, 11, 13—15; from *Chem. Zentr.*, 1919, iii, 149).—Some years ago, one of the authors proposed to replace Gay-Lussac's formula, $v_t = v_0(1 + \alpha t)$, by the expression $v_t - x = (v_0 - x)(1 + \alpha)^t$, or, approximately,

$$v_t = v_0(1 + \alpha)^t,$$

where $\log(1 + \alpha) = 0.00111$. At temperatures above 0° , and within not too narrow limits, the results agree closely with those of Gay-Lussac's formula, but the discrepancies increase with decreasing temperature; at -182° , for example, the ratio of the density to that at 0° is about 3 according to Gay-Lussac and about 2 according to Mewes. Investigations by others have tended to confirm the older formula; the authors have therefore re-examined the behaviour of air, nitrogen, oxygen, and hydrogen with diminishing temperature, and have been led to the conclusion that sources of error are to be found in the previous arrangements of all investigators, including their own. To eliminate such sources (partial liquefaction and surface condensation of the difficultly liquefiable gases), the ratio of the liquid portion to the total amount must be ascertained, which could be accomplished mathematically. It is found, however, that they do not give a satisfactory explanation of the divergencies between the experimental and calculated results; particularly in the case of hydrogen, they

can only exercise a slight influence on the value of the specific heat.
H. W.

The Specific Heat of Air at Ordinary and Low Temperatures. KARL SCHEEL and WILHELM HEUSE (*Zeitsch. Sauerstoff Stickstoff. Ind.*, 1919, **11**, 26—29; from *Chem. Zentr.*, 1919, iii, 148—149).—The previous determinations of the specific heat of air at low temperatures are confined to -77° , -102° , and -170° , and lead to the conclusion that the specific heat at atmospheric pressure is independent of the temperature. The authors' experiments have been performed with a specially constructed calorimeter, in which the loss of heat is reduced to very small dimensions. The apparatus and mode of experiment are fully described in the original. The authors find that the specific heat of air increases with decreasing temperature, and is approximately 5% greater at -183° than at the ordinary temperature.
H. W.

Variation of the Specific Heat during Melting and the Heat of Fusion of some Metals. ITRÔ IITAKA (*Sci. Rep. Tôhoku Imp. Univ.*, 1919, **8**, 99—114).—The specific heats of the elements bismuth, lead, tin, zinc, sulphur, and sodium have been determined at several temperatures, both above and below the melting points. It is shown that the specific heat undergoes a discontinuous change during melting, which is generally positive, but in some cases the change is negative. The following values have been obtained: bismuth, c_s 0.0338, c_l 0.0356, Mc_s 7.02, Mc_l 7.40; lead, c_s 0.0358, c_l 0.0340, Mc_s 7.43, Mc_l 7.04; tin, c_s 0.0662, c_l 0.0615, Mc_s 7.88, Mc_l 7.31; zinc, c_s 0.110, c_l 0.121, Mc_s 7.20, Mc_l 7.91; sulphur, c_s 0.200, c_l 0.199, Mc_s 6.41, Mc_l 6.39; sodium, c_s 0.330, c_l 0.347, Mc_s 7.59, Mc_l 7.98. The specific heat of the solid at the melting point is designated by c_s , that of the liquid at the same temperature by c_l , and the atomic heats by Mc_s and Mc_l respectively. The atomic heat is almost constant and independent of temperature for the liquid elements. The atomic heat at constant volume has been calculated for the temperatures 0° , 100° , 200° , 300° , and the melting point. The values at the melting point are: bismuth 6.90, lead 6.58, mercury 5.90, tin 7.40, and zinc 6.22. The latent heat of fusion has also been calculated from the experimental results, and the following values obtained: bismuth 12.24, lead 5.53, tin 13.38, zinc 23.1, sulphur 13.2, and sodium 26.0.
J. F. S.

Calculation of the Latent Heat of Vaporisation from Critical Data. W. HERZ (*Zeitsch. Elektrochem.*, 1919, **25** 323—324).—By means of the equations $L = p_k \cdot T_k / T_k \cdot d_k$ and $L = 2/3 \cdot p_k / d_k$, the author shows that the latent heat of vaporisation of non-associated liquids may be calculated. The symbols have the following significance: L is the latent heat of vaporisation, T_k is the boiling point in degrees absolute, T_k and p_k the critical temperature and critical pressure respectively, and d_k is the critical density. The calculations have been made for twenty

two organic liquids and three inorganic liquids, and it is shown that there is a moderate agreement between the calculated and experimental results. In the case of water and methyl alcohol, which are associated, there is a wide divergence between the calculated and experimental values, but in that of acetic acid, which is also associated, the two agree to within 10%.
J. F. S.

A Vapour Pressure Equation. GEORGE W. TODD and S. P. WEN (*Phil. Mag.*, 1919, [vi], **38**, 655—660).—A mathematical paper in which the equilibrium of a vapour in contact with its liquid is considered on the assumptions that all vapour molecules striking the liquid surface penetrate it, and only those liquid molecules which have a velocity greater than a definite critical value, whatever their angles of impact with the surface, penetrate it and leave the liquid. Vapour-pressure equations $p = A \rho e^{-B/\theta} (1 + B/\theta)$ and $p = A' e^{-B/\theta} (1 + B/\theta)$ are deduced, in which p is the vapour pressure and ρ the density at a temperature θ . B is the collision frequency of a molecule of velocity c . The former equation is useful where the density values are known up to the critical temperature, and the latter for those cases where the density is only known over moderate ranges of temperature. The equations are tested in the case of water, mercury, benzene, bromine, and ethyl ether, where a fairly good agreement with experiment is found. The average kinetic energy of a molecule at the critical temperature (θ_c) is given by the expression $\frac{1}{2} m c_c^2 = \theta_c / 273 (5.5 \times 10^{-14})$ erg. A table of values of $\log A'$ and B obtained from vapour-pressure measurements is given for thirteen liquids, and it is shown that the value of B obtained from the critical temperature is one-third to one-fourth of the value obtained from the equation.
J. F. S.

Simple Method of Determining the Velocity of Sound in Gases and Vapours and the Density of Gases. P. BRÄUER (*Zeitsch. physikal. Chem. Unterr.*, 1919, **32**, 1—6; from *Chem. Zentr.*, 1919, iii, 114—115).—The experiment is performed in thin-walled tubes, 2—3 cm. in diameter and at most 60 cm. long, which are filled with the gas or vapour. The note emitted when the tube is struck is matched by that of a monochord string, and the experiment is repeated with the tube full of air. The frequencies of the notes are inversely proportional to the lengths of the strings. The velocity of sound and the density of the gas are readily calculated. The procedure is as accurate as that proposed by Victor Meyer, and can be more rapidly carried out.
H. W.

Absolute Determination of the Coefficients of Viscosity of Hydrogen, Nitrogen, and Oxygen. KIA-LOK YEN (*Phil. Mag.*, 1919, [vi], **38**, 582—596).—The absolute viscosities of hydrogen, nitrogen, and oxygen have been determined at 23.00° and 760 mm. pressure by Millikan's constant deflexion apparatus, previously described (Gilchrist, *Phys. Rev.*, 1913, **1**, 124; Harrington, *ibid.*, 1916, **8**, 738). The results obtained are: hydrogen, $\eta \times 10^7 =$

882.16 (20 expts.); oxygen, $\eta \times 10^7 = 2042.35$ (20 expts.); and nitrogen, $\eta \times 10^7 = 1764.80$ (21 expts.). An accuracy of 0.15% is claimed for the results.

J. F. S.

Adsorption of Gases at Low and Moderate Concentrations. I. Deduction of the Theoretical Adsorption Isostere and Isotherm. II. Experimental Verification of the Form of the Theoretical Isosteres and Isotherms. A. M. WILLIAMS (*Proc. Roy. Soc.*, 1919, [A], **96**, 287—297).—The theoretical form of the adsorption isostere is deduced and found to be $\log a/c = B + A/T$, where A and B are functions of a alone. The theoretical form of the adsorption isotherm is found to be $\log a/c = A_0 - A_1 a$, where A_0 and A_1 are functions of the temperature only. These equations are tested by means of the data of various observers on the gases, argon, methane, carbon dioxide, ammonia, nitrogen, and carbon monoxide. A satisfactory agreement is found in the case of the former equation for gases above or near the critical temperature. In the latter case satisfactory agreement is found up to moderate adsorptions of gases above their critical temperature.

J. F. S.

Adsorption of Gases at Low and Moderate Concentrations. III. Experimental Verification of the Constants in the Theoretical Adsorption Isostere. A. M. WILLIAMS (*Proc. Roy. Soc.*, 1919, [A], **96**, 298—311. Compare preceding abstract).—The constants of the equation for the theoretical adsorption isostere are deduced from the observations of many observers for the gases argon, ethylene, carbon dioxide, methane, carbon monoxide, and nitrogen. The form of theoretical adsorption isostere has been determined at zero concentration for the above-named gases above the critical point. The relationship among the constants is in good agreement with the theory based on the existence of a thin surface layer. The range of molecular attraction is determined and found to vary from 3.2 to 4.1×10^{-8} cm.

J. F. S.

Theory of Adsorption of Electrolytes. The Adsorption of Organic Dyes. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1919, **97**, 57—84).—The salts of basic and acid dyes have been employed in the study of adsorption by various substances. In the case of charcoal the cations and anions are adsorbed in equivalent proportions. Slight deviations from this principle can be explained by the impurity of the charcoal. When insoluble salts are used as adsorbents there is an exchange of anions or cations between the adsorbents and the substance adsorbed. Insoluble acid or basic oxides have shown no perceptible adsorbing capacity. In no case was a "hydrolytic" adsorption of the salts observed, that is, where the salts were split into acid and base, and the adsorption of one ion only took place. The nature of the adsorption capacity of carbon is discussed.

S. S. Z.

Adsorption of H- and OH-Ions and the Ions of the Heavy Metals by Charcoal. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1919, **97**, 85—97).—The H- and OH-ions are

adsorbed by charcoal to the same extent. The amount of mercuric chloride adsorbed by charcoal may, in the presence of chlorides, be diminished by as much as 60%.
S. S. Z.

Electrification of Water and Osmotic Pressure. JACQUES LOEB (*J. Gen. Physiol.*, 1919, 2, 87—106).—It is shown for the amphoteric electrolytes, aluminium hydroxide, and gelatin, that in the presence of an acid salt water diffuses through a collodion membrane into a solution of these substances as if its particles were negatively charged, whilst water diffuses into solutions of these electrolytes, when they exist as salts of univalent or bivalent metals, as if the particles of water were positively charged. The turning point for the sign of the electrification of water seems to be near or to coincide with the isoelectric point of these two ampholytes, which is about $2 \times 10^{-5} N$ for gelatin and $10^{-7} N$ for aluminium hydroxide.

Apparently positively charged water diffuses with less rapidity through a collodion membrane into a solution of calcium or barium gelatinates than into a solution of lithium, potassium, sodium, or ammonium gelatinates of the same concentration of gelatin and hydrogen ions, and negatively charged water diffuses with less rapidity through a collodion membrane into a solution of gelatin sulphate than into a solution of gelatin chloride or nitrate of the same concentration of gelatin and hydrogen ions.

If osmotic pressure is defined as the additional pressure on the solution required to cause as many molecules of water to diffuse from solution to the pure water as diffuse simultaneously in the opposite direction through the membrane, it follows that the osmotic pressure cannot depend only on the concentration of the solute, but must also depend on the electrostatic effects of the ions present, and that the influence of the ions on the osmotic pressure must be the same as that on the initial velocity of diffusion. This assumption was tested in experiments with gelatin salts, for which a collodion membrane is strictly semipermeable, and the tests confirmed the expectation.
J. C. D.

Hydrogen and Hydroxyl Ion Equilibria in Solutions. II.

W. LÖFFLER and K. SPIRO (*Helv. Chim. Acta*, 1919, 2, 533—550). Compare Asher and Spiro, *Ergh. Physiol.*, 1909, 8, 254).—From experiments, carried out by the indicator method, on the changes in the hydroxyl and hydrogen-ion concentration in solutions of glycine brought about by neutral substances of physiological importance, such as glycerol, dextrose, and ethylene glycol, it is shown that these substances are capable of forming complex salts. This is seen particularly in the case of glycine. Such solutions, which are non-sensitive to a change in their alkalinity, change their concentration of hydrogen and hydroxyl ions by shaking with animal charcoal in the sense that they approach neutrality. The adsorption by charcoal is to be regarded as a process of solution, and it is shown that a different decomposition of acid salts in aqueous solution is brought about by shaking with animal charcoal. J. F. S.

[Behaviour of Non-aqueous Solutions of Salts.] R. BEUTNER (*Zeitsch. Elektrochem.*, 1919, **25**, 328—329, 329—330, A. THIEL, *ibid.*, 329).—Polemical. Beutner answers Thiel's criticism (this vol., ii, 388) of his paper (this vol., ii, 263). In a second paper Thiel further criticises Beutner's conclusions, and in a third paper Beutner gives a final reply to Thiel. J. F. S.

Crystallisation Phenomena in Formaldehyde-Gelatin Jellies. W. MORLLER (*Kolloid. Zeitsch.*, 1919, **25**, 67—74).—The crystallisation of formaldehyde gelatin jellies has been experimentally studied. It is shown that the crystallisation phenomena (formation of sphæro-crystals) are to be attributed to the orienting influence of the formaldehyde condensation and polymerisation products on the α -gelatin micellæ. In the observed spherical crystal formation the individual micellæ are arranged radially in the form of concentric spherical sheaths, and behave optically as a crystalline drop. The numerous forms which differ from the above are attributed to a deformation brought about by the tensions set up while the jelly is drying, whereby the arrangement of the micellæ approaches more and more to a fibrous structure. Sphæro-crystals produced by varying the experimental conditions often exhibit this fibrous structure. J. F. S.

Coagulation. I. The Velocity of Gelation and Hydrolysis of Gelatin Sol. RINOSUKE SHÖJI (*Biochem. J.*, 1919, **13**, 227—238).—The equation $\eta - \eta_i = \mu t / 1 + (\mu/\lambda)t$ is given, which represents the change in viscosity of gelatin sol with respect to time in the early stages of gelation, and the bearing of this equation on the nature of gelation is discussed at some length.

Another equation, $2k\tau = 1/(\eta_i - \eta_{i\infty})^2 - 1/(\eta_{i0} - \eta_{i\infty})^2$, is given which represents the change in viscosity of gelatin sol with respect to time in the course of its hydrolysis caused by heating.

J. C. D.

Coagulation Process [of Colloids]. H. R. KRUYT and JAC. VAN DER SPEK (*Kolloid Zeitsch.*, 1919, **25**, 1—20).—The coagulation of arsenic sulphide and ferric hydroxide sols has been investigated. It is shown that the relationship between coagulation value and the colloidal concentration for arsenic sulphide sols varies as follows: the coagulation value for a univalent precipitating ion increases with increasing dilution, for a tervalent ion it decreases, and for a bivalent ion there is a slight decrease. The reduction of the degree of dispersion by boiling or by a change in the original concentration leads to an augmentation of the coagulation value for potassium and barium ions, but to a reduction for aluminium ions. These phenomena may be explained by the hypothesis that the colloidal particles may combine as they approach one another through their Brownian movements. The reduction of the total surface conditions a reduction of the quantity of electrolyte necessary to reach a definite adsorbed quantity. Dilution and a reduction in the dispersity cause a separation of the particles and

reduce the chances of their collision, and under these conditions a smaller charge is necessary for their coagulation. Similar experiments were made with ferric hydroxide sol, but here both sodium hydroxide and disodium phosphate behave irregularly. J. F. S.

Colloidal Processes in the Setting of Plaster. Structure of Plaster of Paris. I. TRAUBE (*Kolloid. Zeitsch.*, 1919, 25, 62—66).—The velocity of the setting of the hemihydrate of calcium sulphate has been investigated, and the influence of the addition of salts, acids, bases, and neutral substances to the soft plaster on the rate of setting has been observed. Ten grams of calcium sulphate were rapidly mixed with stated quantities of water or solutions of other substances, the mixture poured on to a glass plate, and the time noted when it had completely set. With 4 c.c. of 0.5*N*-potassium chloride, setting occurred almost instantaneously, with 5 c.c. in 2.5 minutes, with 7 c.c. in 4 minutes, with 15 c.c. the mixture had not set in 40 minutes. Using 7 c.c. of saturated potassium chloride solution, setting occurred in 12 minutes; 7 c.c. of *N*/2-solution required 4.5 minutes, 7 c.c. of 0.25*N* required 5.5 minutes, and 7 c.c. of *N*/16 19 minutes. There is, therefore, a maximum setting velocity for medium concentrations. In experiments with other salts, it is shown that the influence of the anion is very small, but that of the cation is all-important. The order in which the cations influence the setting is the reverse of the order in which they precipitate colloids from solutions; thus the univalent cations accelerate the setting most. From these experiments, it is concluded that the combination of the hemihydrate of calcium sulphate with water is brought about in the first place by gel formation. A similar series of experiments was made with 7 c.c. of various acids in *N*/2-concentration. The order of setting from the most rapid is hydrochloric acid, oxalic acid > sulphuric acid > trichloroacetic acid > tartaric acid > boric acid > phosphoric acid > dichloroacetic acid > chloroacetic acid > acetic acid > propionic acid > citric acid. The addition of 7 c.c. of *N*/2-potassium hydroxide effected setting in about the same time as hydrochloric acid. Non-conductors, such as chloral hydrate, amyl alcohol, propionitrile, mannitol, paracetaldehyde, methyl alcohol, and methyl ethyl ketone had no influence on the rate of setting. Gelatin and gums retarded the rate of setting. By allowing ferric chloride to diffuse through the set plaster towards potassium ferrocyanide which is diffusing in the opposite direction, structures of the same nature as the protoplasm structure are obtained. Agate structures and others of both geological and physiological interest have also been obtained. The author's experiments confirm in every detail the views on the nature of the setting of cements put forward by Cavazzi (A., 1913, ii, 136). J. F. S.

Molecular Mechanism of Colloidal Behaviour. II. The Swelling of Fibrin in Alkalis. RICHARD C. TOLMAN and RUSSEL S. BRACEWELL (*J. Amer. Chem. Soc.*, 1919, 41, 1503—1510. Compare Tolman and Stearn, this vol., ii, 101).—The swelling of

fibrin in solutions of sodium hydroxide, potassium hydroxide, and ammonia of various concentrations, and also of similar solutions containing potassium chloride, potassium sulphate, and sucrose has been investigated. It is shown that the swelling in solutions of sodium and potassium hydroxides reaches a maximum at very low concentrations—less than $N/20$; in the same way, the adsorption of alkali reaches a maximum at low concentrations, and a further increase in the concentration of the alkali brings about no change in the adsorption, but a reduction in the amount of swelling. In the case of ammonia solutions, it is shown that both the amount of swelling and the adsorption increase with increasing concentration up to $0.8N$ without reaching a maximum. The addition of neutral salts reduces the swelling in the same way as increase in the concentration of the alkali itself after the maximum has been reached, and also increases the adsorption. Sucrose has no effect on the swelling of fibrin, but water is adsorbed from the solution by the fibrin.

J. F. S.

Molecular Mechanism of Colloidal Behaviour. III. Chemical Nature of the Adsorption of Acids and Alkalis by the Protein Molecule. RUSSEL S. BRACEWELL (*J. Amer. Chem. Soc.*, 1919, **41**, 1511–1515. Compare preceding abstract).—A theoretical paper in which it is shown that the acid-adsorbing power of proteins is mainly due to the free amino-groups present, that is, adsorption consists in the formation of weak compounds between the amino-group and the acid. Attempts to formulate a similar hypothesis for alkali adsorption were unsuccessful.

J. F. S.

Colour of Colloids. VIII. WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 445–468. Compare this vol., ii, 324).—A continuation of the previously published discussion. In the present paper, absorption colours, colours of turbid media, prismatic dispersion colours, grating colours, and colours of thin films are discussed in their relationships with the colour of birds and butterflies.

J. F. S.

Colloidal Electrolytes: Soap Solutions as a Type. JAMES WILLIAM MCBAIN, (Miss) MARY EVELYN LAING, and ALAN FRANCIS TITLEY (*T.*, 1919, **115**, 1279–1300).

The Degree of Hydration of the Particles which Form the Structural Basis of Soap Curd, Determined in Experiments on Sorption and Salting Out. JAMES WILLIAM MCBAIN and (Miss) MILLICENT TAYLOR (*T.*, 1919, **115**, 1300–1308).

Simultaneous or Successive Chemical Decompositions Provoked by Physical Agents. J. A. MULLER (*Compt. rend.*, 1919, **169**, 793–794).—In simultaneous decompositions of the first order, the ratios of the two coefficients of decomposition, at the end of any given time, are equal to the ratios of the corre-

sponding velocity constants. The subject is discussed mathematically, and the equations given, together with the results of chemical analyses, provide a means of determining the nature and order of the changes produced in pyrogenic decompositions.

W. G.

The Interaction of Chlorine and Hydrogen. The Influence of Mass. DAVID LEONARD CHAPMAN and JOHN REGINALD HARVEY WHISTON (T., 1919, 115, 1264—1269).

Comparison of the Temperatures of Explosion calculated from Specific Heats with the Temperatures of Explosion calculated from Explosive Pressures. HENRI MURAOUR (*Compt. rend.*, 1919, 169, 723—726).—As the result of experiments with mixtures of tolite and ammonium nitrate, it is shown that the explosion temperatures, as calculated from the specific heats of Mallard and Le Chatelier or of Sarrau, are markedly higher than the figures obtained by calculation from the manometric tables, except where the temperatures are above 3000°. The results obtained by either method in the region 1500—1700° are certainly below the actual temperatures. The results, as calculated from the manometric pressure in this region, are so low as to indicate either that the value of the pressure must be modified or that the law used for expressing the compressibility of gases at high temperatures and pressures is incorrect. Over the temperature range 1300—2700° the temperatures, calculated from Schreber's specific heats, are in accord with the temperatures calculated from the pressure tables of the French research laboratories.

W. G.

Ignition of Gases by Hot Wires. W. M. THORNTON (*Phil. Mag.*, 1919, [vi], 38, 613—633).—The ignition of the gases hydrogen, methane, ethane, pentane, ethylene, carbon monoxide, coal gas, and vapours of methyl alcohol, ethyl alcohol, diethyl ether, and benzene in air by electrically heated wires of platinum, nickel, iron, tungsten, molybdenum, gold, and silver of various diameters and at various temperatures has been experimentally investigated. It is shown that ignition by hot wires occurs when the generation of heat per unit length has reached a certain definite value. At low temperatures, this is removed by convection, when a steady state is reached, and is almost independent of the diameter of the wire. Ignition is independent of gas pressure, of the heat of combustion of the mixture, of the proportion of gas present, and for any given metal, independent of the nature of the combustible molecule so far as it is affected by change of diameter, hydrogen and platinum being exceptions. That is, since previous heating of the gas does not affect ignition temperatures, it is, on the whole, independent of every external physical or chemical variable. The source of ignition must therefore be sought in some phenomenon depending strictly on the rate of generation of heat by the passage of the current, but occurring, if not within the surface layer of the metal itself, so near to it that the ordinary gas laws are not

operative. Oxygen is the only active component of all the mixtures, and it can be inferred that the mechanism of hot wire ignition is an attack on oxygen either within the wire or by positive ions of combustible gas just ejected from it, for the temperatures at which surface action begins are lower than those which start combination of gases separately heated to a point at which they explode on mixing. Electric and magnetic fields have no influence on surface combustion observable by the phenomena of ignition. Compared with spark ignition, hot wire ignition is singularly constant in type.

J. F. S.

The Determination of Ignition-temperatures by the Soap-bubble Method. ALBERT GREVILLE WHITE and TUDOR WILLIAMS (Proc. T., 1919, 115, 1248—1264).

Indirect Analysis of Gas Hydrates by a Thermodynamic Method and its Application to the Hydrate of Hydrogen Sulphide. I. and II. F. E. C. SCHEFFER and G. MEYER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 1204—1212, 1338—1348). —In earlier papers (Scheffer, A., 1911, ii, 264, 870) it is shown that in solutions of hydrogen sulphide a four-phase equilibrium exists between a hydrate, two liquid phases (water and hydrogen sulphide), and gas. The analysis of the hydrate leads to a water content between 5.1 and 5.4 molecules per molecule of hydrogen sulphide. It is likely that the accepted value $5\text{H}_2\text{O}$ is not correct, and, with the object of determining the true composition, the authors have developed, on thermodynamical considerations, a method of indirectly ascertaining the composition of such hydrates. The method is briefly as follows. A binary system is taken of which one component, A , is gaseous over a definite temperature range, and the second, B , is near its melting point, and is not markedly volatile. On increase of pressure, a solid compound can form from the gas A and the solid B . In the melted component B , the gas is soluble neither as such nor as compound. In the equilibria set up, the component A appears as a gas (G) and bound in the compound S ; the component B occurs free as solid, S_B , and liquid, L , and bound in the compound S . The three-phase lines $S_B LG$ and $SS_B L$ coincide with the melting-point line of B . The transformation is indicated by the change $S_B \rightleftharpoons L$ on both three-phase lines, and is the same as on the melting-point line of pure B . The triple point of B lies near the T axis; the sublimation and boiling-point line of B practically coincides with the T axis. If the compound is indicated by AB_n , the transformations on the two other three-phase lines are indicated by $AB_n \rightleftharpoons A + nB - E_1$ (on $SS_B G$) and $AB_n \rightleftharpoons A + nB - E_2$ (on SLG). The difference of the two energies E_1 and E_2 is equal to the heat of fusion of n molecules of B . $E_2 - E_1 = nQ$ when the heat of fusion of B is Q per molecule. Making use of the Clapeyron equation, the value of $E_2 - E_1$ can be determined if the three-phase lines $SS_B G$ and SLG are known. This method is applied to the system hydrogen sulphide-water, and the lines $SS_B G$ and SLG are experimentally determined, and from

the data thus obtained the value of n is found to be 6. Hence the crystalline hydrate of hydrogen sulphide is $\text{H}_2\text{S}\cdot 6\text{H}_2\text{O}$.

J. F. S.

Theory of the Velocity of Reaction in Gases. KARL F. HERZFELD (*Ann. Physik*, 1919, [iv], 59, 635—667; *Zeitsch. Elektrochem.*, 1919, 25, 301—304).—A theoretical paper in which the velocity of reactions of the first and second order is discussed mathematically. In an historical introduction, the work of Trautz (A., 1909, ii, 557, 651), among others, is discussed. It is shown that, in developing a systematic conception of gas reactions, the introduction of a retardation is helpful. That is, a condition based on the consideration of whether an atom can react directly or whether it must first break away from an existing combination before reaction is possible. In exothermic reactions with one or no retardation, every collision of the molecules is operative, independently of the temperature, whilst with two retardations only a small fraction of the collisions is operative, and these are dependent on the temperature. In the case of endothermic reactions, only one example of a retardation is known, namely, the formation of hydrogen bromide; here it is shown that, for a collision to be operative, the kinetic energy, which depends on the opposing velocities of the colliding particles, must be greater than the heat of the reaction. The influence of the internal energy makes itself obvious, inasmuch as only a definite proportion of the reacting substances can be converted into the products of the reaction. Therefore in exothermic reactions the number of operative collisions is to be multiplied by a factor which depends on the internal specific heat. The reaction formulæ deduced are applied to the work of Bodenstein (A., 1899, ii, 637) and Lind (A., 1907, ii, 76) on the formation of hydrogen bromide, and very good agreement is shown to exist.

J. F. S.

The Velocities of Combination of Sodium Derivatives of Phenols with Olefine Oxides. II. DAVID RUNCIMAN BOYD and (MISS) DORIS FELTHAM THOMAS (T., 1919, 115, 1239—1243).

The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Water-Acetone Mixtures. GEORGE JOSEPH BURROWS (T., 1919, 115, 1230—1239).

Kinetics of Reactions with Substituted Malonic Acids. A. L. BERNOULLI and W. WEGE (*Helv. Chim. Acta*, 1919, 2, 511—532).—The kinetics of the scission of carbon dioxide by heat from malonic acid or methyl-, ethyl-, allyl-, benzyl-, phenyl-, diallyl-, dimethyl-, methylethyl-, diethyl- and dipropyl-malonic acids have been studied at 100°. The formation of acetic acid from an aqueous solution of malonic acid, over the temperature range 75—110°, is a strictly unimolecular reaction. By means of graphic extrapolation, it is shown that the lower limit of measurable change

lies at 66°. With the single exception of dipropylmalonic acid, in which case the value of k is not satisfactory, it is shown that all the substituted malonic acids are decomposed at 100° in aqueous solution, according to a unimolecular equation. Substituents, in the malonic acids, with either one or more double bonds, increase the velocity of decomposition, whilst substituents without double bonds reduce the rate of decomposition. The accelerating action of the double bond increases with the number and also with the nearness to the methylene group of the malonic acid; thus, the phenyl group accelerates the velocity more than the benzyl group. The entrance of a second substituent, similar or dissimilar, strongly decreases the rate of decomposition; thus, diallylmalonic acid decomposes with about half the velocity of allylmalonic acid. A parallelism is shown between the thermal stability of these substances (measured by the heat of formation) and the kinetic stability (measured by the reciprocal of the reaction velocity).

J. F. S.

The Rhythmic Evolution of Carbon Monoxide and the Constant of Accumulation. TOKIHARU OKAYA (*Proc. Phys. Math. Soc. Japan*, 1919, [3], 1, 43—51).—The author has previously suggested that in the case of the rhythmic precipitation of silver chromate in gelatin, there must exist certain relations between the concentrations of the reacting ions to determine the physical state at the moment of precipitation, and concluded that to precipitate silver chromate it is only necessary that the amount of "accumulation product" of the ions should attain a definite value, H^1 , which is constant throughout. In the present paper, the phenomenon of the rhythmic evolution of carbon monoxide produced by the dehydration of formic acid by sulphuric acid is satisfactorily explained by the notion of the "accumulation product." It is also shown that the reaction is one of the first order. The author points out that the existence of the quanta in natural phenomena is not limited to energy only. The present case and Liesegang's phenomena are but examples of such types of natural phenomena.

CHEMICAL ABSTRACTS.

Size and Shape of the Electron. ARTHUR H. COMPTON (*Physical Rev.*, 1919, 14, 20—40).—Assuming as proved that the amount of radiation of short wave-length scattered by various elements is proportional to the atomic number of the element, and accepting Thomson's assumption that the electron is a point charge, the scattered energy should be as great as that calculated from the Thomson equation. Actually, it is considerably less, sometimes as low as one quarter of the theoretical value. Unless a pulsation theory for these rays is abandoned, the discrepancy can only be explained on the assumption that the electron is comparable in magnitude with the wave-length of the shortest rays, or 2×10^{-10} cm. Three types of electrons are suggested, and the scattering is calculated for each type. All three satisfactorily fulfil the requirements. Type I, rigid spherical shell; type II,

flexible spherical shell; type III, flexible spherical ring. On still another count, a point charge electron is inadequate to account for the fact that emergent scattered radiation is more intense than incident radiation. It is necessary to assume an independent rotational activity of the electron, which type III above seems best suited to admit.

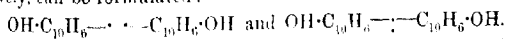
CHEMICAL ABSTRACTS.

Valency Centres. O. HINSBERG (*J. pr. Chem.*, 1919, [ii], 99, 232—238).—An extension of ideas previously advanced (A., 1916, i, 725; 1917, ii, 173, 461; 1918, ii, 106).—The theory deals with the elements of the first, second, fourth, sixth, and eighth groups of the periodic system, and it is assumed that one valency centre is present in the first four elements of each series and two valency centres in the four succeeding elements. The discontinuity of the physical properties of the elements in a series is conditioned by the occurrence of the second valency centre from the fifth group onwards, which causes a marked depression in melting and boiling points. In the formation of compounds with negative elements, the total valency of the elements of the fifth to seventh groups is utilised, whilst with positive elements or groups only the differential valency is used; the occurrence of elements of no valency appears to be merely an extension of the process of equalisation of the valencies of the two centres, the commencement of which is already apparent in the fifth to seventh groups. The ability to form ions, which is proper to many elements of the sixth and seventh groups, is probably due to the tendency of the atoms to form a particularly stable system by internal equalisation, in which four electrons are attached to each nucleus, or eight electrons are contained in a ring. The capability of forming onium compounds, as exhibited by nitrogen, sulphur, iodine, etc., depends on the presence of two valency centres, and therefore occurs solely in the right half of the periodic system. The equivalence of the sulphur atom to the $-\text{CH}:\text{CH}-$ group in the formation of ring compounds (for example, thiophen and benzene) is explained by the formulæ:



in which the two hydrogen atoms of the group $\text{CH}:\text{CH}$ are replaced in the sulphur atom by two valency electrons (E), which are not compensated within the atom.

A number of cases among sulphur compounds are known, in which the isomerism can only be explained with difficulty if the presence of a single valency centre in the sulphur atom is assumed; if, however, two valency centres are present, the difficulty is removed. Thus the isomeric β -naphthol sulphides, m. p.'s 216° and 152° respectively, can be formulated:



The molecular complexity of the metalloids can be explained by

assuming that the partial equalisation of the two valency systems which occurs within the atoms can also take place between different atoms.

H. W.

Isomorphism, Isosterism, and Co-valence. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1919, **41**, 1543—1559).—The octet theory of valency indicates that if compounds having the same number of atoms have also the same total number of electrons, the electrons may arrange themselves in the same manner. In this case the compounds or groups of atoms are said to be isosteric. Such compounds should show remarkable similarity in their physical properties, that is, in those properties which do not involve a separation of the atoms in the molecule. Thus O^{--} , F^- , Ne , Na^+ , and Mg^{++} are isosteric, as also are $N_2 \cdot CO \cdot CN^-$ and CH_4 and NH_4^+ . In cases where isosteric groups have the same electric charges the properties are directly comparable; thus, N_2 and CO , N_2O and CO_2 , KN_3 and $HCNO$ are nearly alike in all their physical properties. When the charges are dissimilar the similarity may manifest itself between properly chosen compounds, thus, KNO_3 and $CaCO_3$. The following cases of crystalline isomorphism are predicted by the octet theory and found to be in accordance with experimental observation: NaF and MgO , KN_3 and $KNCO$, KNO_3 and $SrCO_3$, $KClO_4$ and $SrSO_4$, $NaHSO_4$ and $CaHPO_4$, $MnSeO_4 \cdot 2H_2O$ and $FeAsO_4 \cdot 2H_2O$. Many other pairs are predicted, but have not yet been experimentally investigated. The theory of isosterism makes the deduction of certain relationships a very simple matter. Thus since argon is an isostere of the potassium ion, and methane is an isostere of the ammonium ion, it follows that the potassium and ammonium ions must have similar properties because argon and methane are nearly alike in physical properties. Similarly, the relationship between argon and nitrogen enables the tracing of an equally close relationship between cyanogen and chlorine ions. The experimental data prove that the crystalline form of substances depends on the structure as given by the octet theory, thus indicating that this theory gives a true picture of the constitutions of crystalline solids. The following conclusions are drawn: (1) the co-valency of sodium, potassium and chlorine (in chlorides) is zero. (2) The co-valency of the central atom is 4 in nitrates, carbonates, sulphates, perchlorates, phosphates, permanganates, chromates, selenates, and borofluorides. (3) Carbonates and sulphites are not isomorphous, the co-valency of the central atom being 4 and 3 respectively. (4) Nitrates and chlorates are not isomorphous, the co-valency of the chlorine being 3 in chlorates.

J. F. S.

New Hypotheses as to Different States of Matter. N. T. BACON (*J. Physical Chem.*, 1919, **23**, 469—477).—A theoretical paper in which it is shown that in the solid and liquid conditions matter is virtually incompressible, although under very high pressure, but constantly increasing in volume with increasing temperature, and for the liquid state with this condition continuing up to the critical point, except that near the critical point the apparent

compressibility of the liquid phase may be increased by solution of vapour molecules. The molecule, therefore, is constantly increasing the diameter of its sphere of influence as temperature increases up to the critical point. At this point the spheres of influence of the molecule of liquid and of vapour have the same size, since both forms of matter occupy the same space and have the same density. At the critical point the volatile form is at the dividing line between a saturated vapour and a true gas, and the vapour cannot act as a true gas because the spheres of influence of its molecules are in three dimensional contact, thus precluding translatory motion. Although the molecules in the liquid state continue to increase the dimensions of their spheres of influence with advancing temperature in spite of increasing pressure, nevertheless gaseous molecules can be materially compressed so as to occupy a smaller volume than at the critical point even at temperatures well above the critical temperature. Hence the spheres of influence of a true gas decrease with increasing temperature so as to allow a free path and thus cause them to follow Boyle's Law. The effect of the dissolved barium sulphate in a saturated aqueous solution is considered. Here a single molecule of barium sulphate (that is, one barium ion and one sulphate ion) so influences 10,000,000 water molecules that they are incapable of dissolving more barium sulphate, and imparts to the water a much higher conductivity; all this when the barium sulphate in solution can only come into contact with a small fraction of the water molecules. The author considers that the solution of barium sulphate up to its saturation point brings about a virtual expansion of the water molecules so as practically to fill up all the intermolecular spaces in the solvent and consequently leave no further room for additional barium sulphate. The conductivity of the barium sulphate solution he attributes to the barium sulphate breaking up into an enormous number of electrons, each having the characteristic periodicity of barium sulphate, and these so permeate the solvent that each molecule of this is in some way in contact, periodically at least, with such particles, so as to maintain an equilibrium relation. In the case of hydrolysis the complicated periodicity of the salt becomes too extended, so that part of the solute loses coherence and the fractions revert to their simpler, although related, periodicity, each in its own condition as if the other were not present. J F. S.

Automatic Mercury Pump, with Device for Collecting the Aspirated Gases. A. BEUTELL and P. OBERHOFFER (*Chem. Zeit.*, 1919, 43, 705—706).—In the mercury pump previously described (A., 1911, ii, 105) the authors have introduced a vessel at the base of the tubes for collecting the gases drawn off, which are then passed into a measuring burette and an Orsat gas-analysis apparatus. The speed of the pump has been increased by allowing the mercury to drop through two tubes, and the device for preventing fracture of the tubes by the falling mercury has been modified.

W. J. W.

Inorganic Chemistry.

Reaction between Hydrogen and Bromine. J. A. CHRISTIANSEN (reprint from *D. K. Danske Videnskabernes Selskat, Math. fys. Medd.*, 1919, 1, 14).—A theoretical paper in which it is shown from the experiments of Bodenstein and Lind (A., 1907, ii, 76) on the formation of hydrogen bromide that the reaction occurs as a result of the following changes: $\text{Br} + \text{H}_2 = \text{HBr} + \text{H}$ (primary reaction) and $\text{H} + \text{Br}_2 = \text{HBr} + \text{Br}$ or $\text{H} + \text{HBr} = \text{H}_2 + \text{Br}$, and consequently the dissociation of hydrogen bromide takes place with the reaction $\text{Br} + \text{HBr} = \text{Br}_2 + \text{H}$ as the primary change, and is followed by the same secondary reactions as above. It is also shown that the existing experimental data do not exclude the possibility of the formation and dissociation of hydrogen iodide according to the same scheme. The numerical results of Bodenstein and Lind have been used to calculate the critical energy of the process $\text{Br} + \text{HBr} = \text{Br}_2 + \text{H}$ and the value 43,700 cal. obtained. The results are generally considered, and it is concluded that in respect of the heat of dissociation of hydrogen, Langmuir's value, 84,000 cal. (A., 1915, ii, 249), is probably not irreconcilable with Bohr's theoretical value, 62,000 cal. (A., 1913, ii, 1045). A method of illustrating the above-mentioned reaction by means of models of atoms and molecules similar to those of Bohr is indicated. J. F. S.

Periodic Acid and Periodates. ARTHUR ROSENHEIM and ELSE LOEWENTHAL (*Kolloid. Zeitsch.*, 1919, 25, 53–60).—The periodates of sodium, lithium, ammonium, and guanidine have been investigated. The hydrogen-ion concentration of *N*/20-solutions of H_5IO_6 , NaH_4IO_6 , and $\text{Na}_2\text{H}_3\text{IO}_6$ was determined by Sørensen's indicator method with the object of finding the most suitable indicator for use in titrating periodic acid with sodium hydroxide. The hydrogen-ion concentrations found are respectively 6×10^{-3} , 4.05×10^{-7} , and 6.5×10^{-10} . It is shown that, using methyl-orange as indicator, periodic acid can be quantitatively converted by titration into NaH_4IO_6 , and that using thymolphthalein as indicator it is converted into $\text{Na}_2\text{H}_3\text{IO}_6$. The solubility of $\text{Na}_2\text{H}_3\text{IO}_6$ is determined at various temperatures, and the following values in grams per 100 grams of solution obtained: 0°, 0.104; 25°, 0.157; 40°, 0.187; 100°, 0.434. Shaking with 10*N*-sodium hydroxide solution converted this salt into $\text{Na}_3\text{H}_3\text{IO}_6$. A number of experiments, designed to ascertain whether the sodium periodates adsorb sodium hydroxide, were carried out at 17° by shaking periodic acid with a concentrated solution of sodium hydroxide. The experiments show that neither of the sodium periodates mentioned exhibit any colloidal properties, and that these are the only sodium periodates capable of existence in aqueous solution. On the addition of 1 mol. of periodic acid to 2 mols. lithium hydroxide solution a white precipitate is formed which immediately dissolves; the solution, on warming, yields a

white precipitate consisting of microscopic spherules, which on analysis is shown to consist of $\text{Li}_3\text{H}_2\text{IO}_6$. The mother liquor on keeping deposits small, white, six-sided bipyramids of $\text{Li}_3\text{H}_2\text{IO}_6$. Attempts to prepare LiIO_4 and Li_5IO_6 , compounds described by Rammelsberg, failed. The two lithium salts were examined as to the power of adsorption as in the case of the sodium salts, and it is shown that absorption compounds are formed up to the ratio $\text{Li}_2\text{O}/\text{I}_2\text{O}_7 = 5.39$. The two ammonium periodates $(\text{NH}_4)_2\text{H}_2\text{IO}_6$ and NH_4IO_4 , previously described by Rammelsberg (*Ann. Phys. Chem.*, 1868, **134**, 379) were obtained, and a further compound, $(\text{NH}_4)_3\text{H}_2(\text{IO}_6)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, was also obtained. The last compound was prepared in rectangular crystals by shaking periodic acid with an excess of 25% ammonia at 140° for several hours. Two guanidine periodates, $(\text{CN}_3\text{H}_3)_3\text{H}_2\text{IO}_6$ and $(\text{CN}_3\text{H}_3)_2\text{H}_3\text{IO}_6$, were obtained by treating periodic acid with guanidine. Both substances are very sparingly soluble, white, crystalline compounds. The molecular conductivity, boiling point, and freezing point of a number of solutions of periodic acid have been determined. The conductivity determinations show that periodic acid is of medium strength, whilst the boiling-point determinations indicate that it dissociates into two ions, and the freezing-point determinations show that a 5% solution is much less dissociated, and that in a 12–20% solution polymeric periodic acid molecules are present. In general, the work shows that there is a decided, if not very far-reaching, analogy between periodic acid and the periodates on the one hand and telluric acid and the tellurates on the other.

J. F. S.

Flame Reactions of Selenium and Tellurium. HARRY B. WEISER and ALLEN GARRISON (*J. Physical Chem.*, 1919, **23**, 478–497. Compare A., 1914, ii, 317, 398; also Papish, this vol., ii, 105).—The luminescence and the nature of the deposits produced when selenium and tellurium are introduced into various flames have been experimentally examined. The flames used were: air–hydrogen, bunsen, hydrogen–air, and chlorine–hydrogen; the effect of cathode rays on sulphur, selenium, and tellurium was also examined. It is shown that the reaction from selenium to selenic salt produces a blue luminescence, which is the most characteristic in flames containing selenium. It is probable that this luminescence is due chiefly to the reaction from selenic ion to unionised selenic salt. The reaction from tellurium to tellurous salt produces a green luminescence; and from tellurous salt to telluric salt a blue luminescence. It is probable that the green luminescence is due chiefly to the reaction from tellurous ion to the unionised tellurous salt; and the blue luminescence from telluric ion to the undissociated telluric salt. Under certain conditions a red luminescence occurs in flames containing selenium, which is, as a rule, less intense than the blue luminescence. Since the vapours of both elements are coloured, it is probable that the red coloration in both cases is due in part to the colour of the vapours, in part to a purely thermal luminescence, and in part to some stage of the chemical reaction from the vapour of the element to the quadrivalent ion. A green

tip in the flames in air charged with selenium and tellurium compounds is not a luminescence, but is due to the green colour of the vapour of the dioxide, which appears greener by reflecting the blue luminescence just below.

J. F. S.

The Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water. II. W. E. ADENEY and H. G. BECKER (*Sci. Proc. Roy. Dublin Soc.*, 1919, **15**, 609—628).—

The work previously recorded (compare this vol., ii, 104) has been continued with the object of reducing the observations to unit area and volume, and has been extended to include oxygen and nitrogen as pure gases. The apparatus used has also been modified so as to obtain a better temperature control and to eliminate any errors arising from the temperature and vapour pressure of the replenishing gas. A formula is given in each case for oxygen, nitrogen, and air, from which it is possible to calculate the rate of solution of the gas dealt with for any conditions of area exposed, depth, or degree of saturation, provided that the water is kept uniformly mixed.

W. G.

Triatomic Nitrogen, N_3 . MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1919, **25**, 297—300).—A mathematical paper, in which it is shown that at all temperatures above that of liquid air the predominating constituent of active nitrogen (Strutt, T., 1918, **113**, 200) is triatomic nitrogen, N_3 . The concentration of this substance in active nitrogen is represented by its partial pressure, 0.002 mm. The heat of formation from N_2 and N has a maximum value of 5000—10,000 cal. It is therefore, at ordinary temperatures, so much more stable than a mixture of N_2 and N that the decomposition $N_3 + N = 2N_2$ increases because of the relatively large increase in the concentration of triatomic nitrogen with falling temperature. In this fact the irregular temperature-coefficient finds its meaning. Since the cooling of active nitrogen by liquid air does not occur instantaneously, the triatomic nitrogen and the trimolecular destruction of active nitrogen, at temperatures above that of liquid air, predominate over the monatomic nitrogen and its binary compound N_3 . The velocity constant of the third order is of the dimension 10^{17} mol./c.c. as a maximum, and can be much smaller if the third order reaction predominates only at ordinary temperatures. The deactivating of active nitrogen with falling temperature may either pass through a minimum or it may reach a maximum, $k/K = 10^{36}$, which is in keeping with the very large inverse of the temperature-coefficient. Where the triatomic nitrogen preponderates over the monatomic nitrogen at low temperatures above that of liquid air, hexatomic nitrogen must of necessity be formed in the mixture, in quantities which are very small compared with the triatomic nitrogen. The small heat of formation of triatomic nitrogen which is deducible from the very large reaction velocity and is in keeping with the ineffectual attempts to prepare it pure, indicates that it is impossible to prepare this substance pure by thermal methods alone. For on cooling it reacts with monatomic nitrogen to form diatomic nitrogen, and on warm-

ing it decomposes into monatomic nitrogen and hexatomic nitrogen. It is extremely probable that triatomic nitrogen is an open-chain molecule, and that similar triatomic molecules of oxygen, chlorine, bromine, and iodine can also exist, whilst a similar hydrogen molecule cannot exist. The open-chain structure for triatomic nitrogen is indicated by the nitride formation and by the absence of azide formation. The triatomic oxygen will be an isomeride of ozone.

J. F. S.

The Discovery of Phosphorus Two Hundred and Fifty Years Ago. HERMANN PETERS (*Prometheus*, 1919, 30, 249—251, 259—261; from *Chem. Zentr.*, 1919, iii, 111).—Evidence is adduced to show that Hennig Brand is the sole discoverer of phosphorus, and that the rapid spread of the knowledge of the method of preparation is due to Leibniz. The discovery was made in 1669. The application of phosphorus to technical purposes was hindered at first by its high price. The latter was greatly reduced about a hundred years later, when phosphorus was extracted from bone ash by P. Gahn and Scheele. The first phosphorus matches, the so-called Turin candles, were introduced into commerce at the end of the eighteenth century. At the beginning of the nineteenth century the first phosphorus-sulphur matches were made on a small scale, but the actual production of phosphorus matches dates from about 1833. Johann Kunckel's claim of the independent discovery of phosphorus is unfounded, and was disputed by Leibniz. H. W.

Separation by Solidification of Pure Carbon Dioxide from a Gaseous Mixture. V. CRÉMIER and A. LÉPAPE (*Compt. rend.*, 1919, 169, 654—655).—Carbon dioxide may be obtained in a pure, solid state from a gaseous mixture rich in that gas either by allowing the compressed gas to expand suddenly from a narrow orifice through a cloth bag into the air or by compressing the mixture slightly in a vessel cooled to -80° . The solid carbon dioxide is, in either case, free from radium emanation when the latter is present in the original mixture. W. G.

The Effect of Sea-salt on the Pressure of Carbon Dioxide and Alkalinity of Natural Waters. EDMUND BRYDGES RUDHALL PRIDEAUX (*T.*, 1919, 115, 1223—1230).

The Solubility of the Inert Gases in Liquids. ANDREAS VON ANTROPOFF (*Zeitsch. Elektrochem.*, 1919, 25, 269—297).—The solubility of helium, argon, neon, krypton, and xenon has been determined in water at various temperatures, and the solubility of krypton has been determined in pentane, acetic acid, and aniline. Several pieces of apparatus are described which are specially designed for working with the inactive gases. These include (1) a simplified and improved form of the Toepler mercury pump; (2) an absorption pipette, which enables an absorbing liquid or solution to be introduced into a gas contained over mercury, and to be withdrawn again without loss of gas; (3) an apparatus for solubility deter-

minations, in which neither the liquid nor its vapour comes into contact with taps, and (4) a burette in which the gas can be expelled from solution, and which allows of a definite amount of liquid being introduced into the solubility apparatus. The original should be consulted for details and dimensions of the apparatus. The helium used in the experiments was obtained by heating cleveite at 1000° in a porcelain tube, and the product purified in the usual way. The following solubilities (β) in water were obtained: 0°, 0.00967; 10°, 0.00991; 20°, 0.00996; 30°, 0.01007; 40°, 0.01029; 50°, 0.0108. These figures are about 40% smaller than the values found by Estreicher (A., 1900, ii, 205). Argon, krypton, and xenon were separated by a method similar to that of Ramsay and Moore (T., 1908, 93, 2181). The following solubility values in water were obtained: Neon, 0°, 0.0114; 10°, 0.0118; 20°, 0.0147; 30°, 0.0155; 40°, 0.0217; 50°, 0.0322. Krypton, 0°, 0.1095; 10°, 0.0807; 20°, 0.0626; 30°, 0.0511; 40°, 0.0433; 50°, 0.0383; 60°, 0.0357. Xenon, 0°, 0.2200; 10°, 0.1580; 20°, 0.1109; 30°, 0.0893; 40°, 0.0745; 45-45°, 0.0663. In pentane, xenon has the following absorption coefficients: 11.7°, 0.1686; 20°, 0.1335; 25°, 0.1272; 30°, 0.1609; 40°, 0.0949; 49.5°, 0.1084; in aniline, the solubilities per gram are: 10°, 0.6687; 20°, 0.5006; 30°, 0.4426; 40°, 0.4336; 50°, 0.3892. The solubility of the inert gases in water increases with the molecular weight, and in the case of the heavier gases, neon, xenon, krypton, and argon, decreases with increasing temperature. The solubility of helium is practically independent of temperature, whilst that of neon increases rapidly with increasing temperature.

J. F. S.

Solubility of Calcite in Sea-water in Contact with the Atmosphere and its Variation with Temperature. ROGER

C. WELLS (*Carnegie Inst. Publication*, 1918, No. 213 [*Papers from Dept. Marine Biology*, 9, 316-318]).—Certain equilibria, the attainment of which would be expected from experiments in the laboratory, do not seem to be fully attained under natural conditions in the ocean. The equilibria referred to involve the effect of temperature on the exchange of carbon dioxide between sea-water and the atmosphere and the precipitation or solution, as the case may be, of various solid constituents from or into sea-water. Apparently the adjustments occur so slowly, and the bulk of the ocean is so great, with reference to the surface exposed to the atmosphere, that the expected variations with temperature do not appear in the water of the open ocean. Sea-water in contact with an excess of calcite was agitated by a current of outdoor air for forty days, and the dissolved carbonates were estimated at intervals by titration with 0.02N-sodium hydrogen sulphate, using methyl-orange as an indicator. Experiments were made at 1° and at the ordinary temperature (25° to 29°). The colder sea-water tended to retain more carbonate in solution than warmer sea-water, but did not dissolve fresh calcite. Ordinary sea-water appears to contain so much carbonate that in contact with the atmosphere at 1° it

neither has nor acquires an appreciable solvent action on calcite. At higher temperatures, it undergoes a slow diminution in its content of carbonates on being agitated in contact with outdoor air.

CHEMICAL ABSTRACTS.

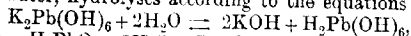
Gravitational Attraction and Uranium-Lead. ANDERS

BULL (*Science*, 1919, 50, 69-70).—No one has satisfactorily explained the discrepancies between the atomic weight of ordinary lead and that of lead from uranium minerals. It is suggested that a difference may exist in their behaviour towards the force of gravitation. Deviations in the value of gravitational acceleration might be proportional to variations in their atomic weight, which would make the atomic mass of all kinds of lead identical. Assuming, finally, that the gravitational attraction is due to electrons, variations in atomic weight might be ascribed to electronic tension set up in the atom by radioactive disintegration and gradually diminishing in the end-product of the series.

CHEMICAL ABSTRACTS.

Critical Study of the Potassium and Sodium Double Salts of Lead Tetrafluoride as Sources of Fluorine.

GEORGE L. CLARK (*J. Amer. Chem. Soc.*, 1919, 41, 1477-1491).—An investigation of the methods of preparation and properties of the double salts formed by lead tetrafluoride with sodium and potassium fluoride respectively, with the object of finding a suitable substance for the preparation of fluorine. *Tripotassium lead hydrogen octafluoride*, $3\text{KF}\cdot\text{HF}\cdot\text{PbF}_4$, is prepared by adding potassium plumbate in small quantities to a concentrated aqueous solution of hydrofluoric acid until a separation of lead dioxide occurs. The solution is filtered through paper supported by several layers of cloth, and the filtrate evaporated slowly in lead dishes on a sand-bath in a gentle current of air until a separation of crystals occurs. The solubility of this salt has been determined in the presence of hydrofluoric acid and potassium fluoride. In the absence of acid, hydrolysis occurs, with the separation of lead dioxide. When heated at 250° , the hydrogen fluoride molecule is expelled, and at temperatures above 250° fluorine is driven off. *Potassium plumbate*, $\text{K}_2\text{PbO}_3\cdot 3\text{H}_2\text{O}$, is best prepared by mixing three molecules of potassium hydroxide with 20% of its weight of water, raising the temperature to 100° , and adding one molecule of lead dioxide; action at once occurs, and the plumbate is formed without decomposition products. This salt is regarded as the dipotassium salt of orthoplumbic acid, $\text{K}_2\text{Pb}(\text{OH})_6$, and, on treatment with water, hydrolyses according to the equations



$\text{H}_2\text{Pb}(\text{OH})_6 = \text{H}_4\text{PbO}_4 + 2\text{H}_2\text{O}$. In the presence of 20% of water, the hydrolysis proceeds so far that hydrated lead dioxide is precipitated. *Disodium lead heptafluoride*, $2\text{NaF}\cdot\text{PbF}_4$, is prepared by the addition of sodium plumbate to aqueous hydrofluoric acid, and crystallisation of the product from hydrofluoric acid to separate sodium hydrogen fluoride. The crystals occur in stout, short plates

which are hydrolysed by water. The solubility has been determined in water containing hydrofluoric acid and sodium fluoride, and is shown to decrease with increasing concentration of hydrogen fluoride until sodium hydrogen fluoride is formed, and then it increases in solubility with an increase in the concentration of hydrogen fluoride. This salt liberates fluorine at 250°. *Sodium plumbate*, $\text{Na}_2\text{PbO}_3 \cdot 6\text{H}_2\text{O}$, is prepared by mixing 150 grams of sodium hydroxide with 50 c.c. of water at 100°, adding lead dioxide until a paste is formed, then adding 25 c.c. of water and lead dioxide to make a total quantity of 300 grams of the latter substance. This salt is much less stable and more easily hydrolysed than the potassium salt. The analysis of the double fluorides is effected in the following manner. The salt is dissolved in water, when hydrolysis occurs, thus: $2(3\text{KF} \cdot \text{HF} \cdot \text{PbF}_4) + 4\text{H}_2\text{O} = 6\text{KF} + 10\text{HF} + 2\text{PbO}_2$; the lead dioxide is filtered off in an alundum crucible, dried at 105°, and weighed. The filtrate is made up to a known volume; in one portion, the free acid is estimated by titration, and in another the potassium fluoride is estimated by evaporation to dryness and ignition at 500°. The two double fluorides are considered as sources of fluorine. The potassium salt is more easily prepared and is more stable than the sodium salt, and, weight for weight of materials used, the potassium salt is twice as efficient as the sodium salt.

J. F. S.

Colloidal Tricalcium Aluminate. A. J. PHILLIPS (*J. Amer. Ceram. Soc.*, 1919, 2, 708—742).—Pure amorphous, calcined, and finely ground tricalcium aluminate forms a true colloidal sol in water, an insignificant proportion of the substance entering into true solution. The crystalline form appears to be highly polymerised, and in contact with water behaves like a colloid, but if suspension is incomplete, the residue may consist of hydrated crystals. A more concentrated suspension is obtained by using lime-water instead of pure water, and the product does not diffuse or dialyse, shows the Tyndall cone, is positively charged, is not coagulated by heat, but is coagulated by freezing, has a high adsorptive power, and generally resembles the well-known sols of ferric, aluminium, and chromic oxides. It does not form a gel on evaporation or by dehydration over sulphuric acid, the product in each case being a loose powder. The lime:alumina ratio in the filtered suspensions never corresponded with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, lime always being deficient, but to an irregular extent, varying with the time, from 1:1.096 after three hours to 1:1.519 after twenty-eight days. The deficiency in the lime is attributed to the free lime being adsorbed by the colloidal aluminate.

The colloidal aluminate is an anhydride which, by capillary attraction, endosmose and molecular imbibition, swells, forming an emulsoid. On the first addition of water to the aluminate, there is a development of heat—due to the formation of an exothermic hydrate. The aluminate is more soluble in cold than in hot water, so that if it is first exposed to moist air and then mixed with water, the conditions favour a great concentration of aluminate in true

solution, this being accompanied by an endothermic change. There is a further development of heat resulting from the disturbance of the equilibrium $(H_2O)_n \rightleftharpoons nH_2O$ of the water-molecules. This is also eliminated when the aluminate has previously been exposed to moist air. When there is a sufficient concentration of cations to disperse the hydrated aluminate as fast as it is formed, the resultant heat effects are either zero or negative, as this dispersion is accompanied by an absorption of heat. The treatment of the colloidal gel only changes the composition of the outer surface; any ionic activity is confined to the surface, except when the film is ruptured, and is a characteristic adsorption effect.

A greater dispersion of aluminate occurs in lime-water than in pure water, as the calcium ions of the calcium hydrate are adsorbed more than the hydroxyl ions by the hydrated aluminate, and when a sufficient number of ions has been adsorbed, their charges and those of the aluminate repel each other, and the aluminate is thereby dispersed.

Any water adsorbed is compressed in the process, any salts in solution being similarly compressed, and their solubility is increased.

As the aluminate can only adsorb a limited amount of cations, when the concentration of the anions is sufficiently increased, the positive charges on the aluminate will be neutralised by the adsorption of the anions because of their increased concentration, and uncharged aluminate is precipitated. The adsorbing surface is decreased, and the ions previously held by adsorption are returned to the solution and exercise a dispersive effect on undispersed material. Hence the concentration of negative ions is greatly increased. A much weaker solution of sodium hydroxide shows the same precipitating effect.

When a smaller amount of water is used, as in preparing cement pastes, the aluminate is converted into a colloidal gel which persists for at least twenty-four hours. On continuing the mixing of the aluminate and water for several minutes, a considerable retardation occurred in the time of setting, but by increasing the percentage of hydrate, so that the total ion-concentration exceeded the adsorptive capacity of the aluminate for cations, the time of setting was reduced. A semipermeable film is formed around the grains of aluminate, which is destroyed on mechanical agitation, a sol being formed at the same time.

On stirring a mixture of equal weights of the aluminate and water, and then slowly adding a volume of hydrochloric acid (D 1.21) equal to that of the water, continuing the stirring and keeping the vessel cool, the viscous paste soon solidifies, and, on keeping, synoresis occurs, an aqueous layer separates, and solidifies to a clear gel containing both alumina and lime.

The rate of coagulation of the aluminate gel is thus affected by the amount of dispersion effected, the synoresis of the gel, the neutralisation of previously adsorbed calcium ions by hydroxyl ions, and the adsorption of undissociated salt. [See also *J. Soc. Chem. Ind.*, 1919, 904A.]

A. B. S.

Rôle of Water of Crystallisation and the Structure of Alums. CLEMENS SCHAEFER and MARTHA SCHUBERT (*Ann. Physik.*, 1919, [iv], **59**, 583—588).—Polemical. It is shown that the crystal model of alum put forward by Vegard and Schjelderup is not correct (A., 1918, ii, 156). It is maintained that the rôle allotted to the water of crystallisation in the crystalline structure of alums by Vegard was put forward by the present authors two years previously (A., 1916, ii, 505). The authors therefore claim priority in this matter. J. F. S.

Amalgams. II. Colloidal Gold Amalgam. C. PAAL and HERMANN STEYER (*Kolloid Zeitsch.*, 1919, **25**, 21—26. Compare this vol., ii, 69).—The gold amalgam sol previously described, on keeping, is oxidised to some extent by atmospheric air; this partly oxidised sol has a somewhat browner solution than the sol when freshly prepared, but may be brought back to its original colour by the addition of a few drops of hydrazine hydrate solution. A small quantity of the sol was kept in solution for twenty-two weeks with the object of determining its stability. It was found that the colour became more fiery-red and that a heavy, grey gel separated. The remaining solid was dried in a vacuum and gave a blackish-violet substance, which was in the form of lamellæ with a bronze tinge; it was completely soluble in water, and had the composition $\text{AuHg}_{0.34}$. The gel contained 5.32% of lysalbic acid, which was used as a protecting colloid, and had the composition $\text{AuHg}_{0.9}$. The gel was non-reversible on warming with either sodium hydroxide or ammonia solution. A number of other experiments are described on the stability of the colloid. J. F. S.

Mineralogical Chemistry.

A Lead-grey, Fibrous Mineral from Binn, Switzerland. R. H. SOLLY. With a chemical analysis by G. T. PRIOR (*Min. Mag.*, 1919, **18**, 360—362).—Fine, acicular crystals associated with seligmannite, and sometimes grouped as triangular lattices in cavities of the dolomite, resemble in their cleavage, colour, and chocolate-coloured streak the several thioarsenites of lead (liveingite, rathite, baumhauerite, and dufrenoyite) found at this locality. Goniometric measurements in the prism-zone, the only one developed, accord more closely with the angles of dufrenoyite, whilst the analysis corresponds with rathite, $3\text{PbS} \cdot 2\text{Sb}_2\text{S}_3$. The presence of thallium is of interest (compare A., 1918, ii, 323).

Pb.	Ag.	Cu.	Tl.	Fe.	As.	Sb.	S.	Insol.	Total.	D ₅ [°] .
51.11	0.76	0.10	0.23	0.21	23.37	0.74	23.22	0.24	99.98	5.453

L. J. S.

Semseyite from Dumfriesshire. G. F. HERBERT SMITH. With a chemical analysis by G. T. PRIOR (*Min. Mag.*, 1919, 18, 354—359).—Specimens of ore from the old antimony-lead mine at Glendinning in Eskdale show small cavities with a drusy lining of minute, iron-black crystals of a thioantimonite of lead. The associated minerals are stibnite, valentinite, ankerite, calcite, blende, and pyrites. The crystals are monoclinic with constants ($a:b:c=1.1356:1.10218, \beta=74^\circ 14'$) somewhat different from those previously determined for plagiönite and semseyite; but the following analysis of the drusy lining, together with the underlying massive material, agree with the semseyite formula, $9\text{PbS}_4\text{Sb}_2\text{S}_3$.

Pb.	Sb.	S.	Fe.	Zn.	CaCO ₃ .	MgCO ₃ .	Insol.	Total.	Sp. gr.
52.37	25.49	18.81	0.67	traces	1.66	traces	0.81	99.81	5.84

L. J. S.

Ferrazite, a New Associate of the Diamond. T. H. LEE and LUIZ FLORES DE MORAES (*Amer. J. Sci.*, 1919, [iv], 48, 353—354).—Some dark yellowish-white pebbles ("favas") from the Brazilian diamond deposits gave the following results on analysis. After deducting silica and alumina as kaolinite and wavellite, the formula is $3(\text{Pb,Ba})\text{O} \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$. Thin sections under the microscope show a granular structure, D 3.0—3.3:

PbO.	BaO.	CaO.	Al ₂ O ₃ .	P ₂ O ₅ .	SiO ₂ .	H ₂ O.	Total.
45.63	8.87	traces	3.48	26.24	2.44	14.20	100.86

L. J. S.

Crystallography of Vogtite, an Anorthic Metasilicate of Iron, Calcium, Manganese, and Magnesium, from Acid Steel-furnace Slags. A. F. HALLIMOND (*Min. Mag.*, 1919, 18, 368—372).—Acid steel-furnace slags consisting mainly of FeO, MnO, and SiO₂ yield the silicates fayalite and rhodonite; but when the amount of lime exceeds about 8% the new silicate *vogtite* separates as long, blade-like crystals. The composition of these is given under I, agreeing approximately with $(\text{Fe,Ca,Mn,Mg})\text{SiO}_3$; II gives the composition of the slag. The crystals are anorthic, $a:b:c=1.093:1.0729, \alpha=99^\circ 37', \beta=99^\circ 21', \gamma=83^\circ 53'$, with perfect cleavages parallel to $M(110)$ and $m(110)$. Optical determinations are given; $B=1.701, 2V_n=65\frac{1}{2}^\circ$, optically negative. The crystals, when free from included glass, are transparent and pale amber-yellow in colour:

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	TiO ₂ .	Total.	Sp. gr.
I.....	47.4	0.15	2.7	15.95	12.95	15.1	5.26	0.10	99.61	3.39
II.....	47.9	1.72	1.2	20.85	10.8	13.0	3.89	0.58	99.4	—

Vogtite differs in density and optical orientation from pyroxman-gite (A., 1913, ii, 869) and sobralite (this vol., ii, 165). L. J. S.

The Role of Boron in Silicates; G. CESARO (*Riv. Min. Crist.*, Ital., 1918, 50, 3—31).—The compositions of borosilicate minerals are discussed, and it is shown that in every case the function of boron is best explained as that of an acid. Datolite is accordingly

an acid metasilicate of calcium, with some silicon replaced by " (B_2O_3) ." Homilite is similar, containing also iron. Euclase corresponds with datolite with aluminium instead of boron, and glucinum instead of calcium. A table is given showing the existence in minerals of acids of boron corresponding with each of those of silicon. Axinite is a combination of di-ortho- and meta-silicates, or a basic triple metasilicate, with B_2O_3 -replacements. Tourmaline is an orthosilicate with part of the silicon replaced by B_2O_3 . Danburite is a neutral tricalcium metasilicoborate. Howlite is an orthosilicate with replacement. In addition to these, the natural borates can be expressed by structural formulæ. The possible constituents of boron acids are discussed.

CHEMICAL ABSTRACTS.

Analytical Chemistry.

Tincture of Muscari as an Indicator. E. DUFILHO (*Bull. Soc. Pharm., Bordeaux*, 1918, 4, 202; from *Ann. Chim. anal.*, 1919, [ii], 1, 325—326).—An alcoholic extract of muscari flowers (grape-hyacinth) may be used as an indicator in acidimetry, the colour change being from red in acid solution to green in alkaline solution. It behaves like litmus in the case of mineral acids, oxalic acid, alkalis and ammonia, and like methyl-orange with phosphoric acid; it is not affected by boric acid except in the presence of glycerol.

W. P. S.

Coloured Indicator Papers. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 175—187).—An examination of the sensitiveness of indicator papers with reference to the quality of the paper itself and its pre-treatment with acid, alkali, or aluminium hydroxide; the nature of the colouring matter used, and its concentration on the paper. Sized papers are less sensitive than unsized, although the reaction on the former is sharper. Otherwise the kind of paper used, and any previous treatment it may have had, are of little importance. The most sensitive Congo paper was obtained by treating filter paper with a 0.1% solution of the dye. This indicated an acidity of 0.0001*N*-hydrochloric acid. The most sensitive paper for strong acids and bases is prepared from a 0.1% solution of azo-litmin.

W. S. M.

Titration of Acids by the Conductivity Method. P. A. MEERBURG (*Chem. Weekblad*, 1919, 16, 1338—1347).—In the titration of various acids with alkalis the author has determined the neutralisation point by a conductivity method. If a graph is plotted in which the abscissæ are represented by c.c. of 0.86*N*-sodium

hydroxide and the ordinates by the values $(1000 - a)/a$, the neutralisation point will be indicated by a definite bend in the curve. With a strong acid and base this bend will be sharp, but it will be obtuse in the case of a weak acid and strong base. With acids and bases having a dissociation-constant, $K > 10^{-10}$, the neutralisation point is readily determined (Dutoit and Duboux, "L'analyse des vins par volumétrie physico-chimique," 54), but if hydrolysable salts are formed the curve becomes continuous and the neutralisation point is masked. In titrating a mixture of two acids having widely differing degrees of ionisation, for example, hydrochloric acid and phenol, the neutralisation of the hydrochloric acid takes place first and is indicated by the lowest portion of the curve, a sharp bend then denoting the neutralisation of the phenol. When the acids have the same ionising power, the method fails, as the lowest point on the curve cannot be accurately determined. Accurate results are obtainable in cases where the relative proportions of the stronger acid to the weaker are 1:1 or 1:2.5, but when the proportions were 2.5:1 the author found the results too low for the strong acid and too high for the weaker one. Tables and curves are given for various acids, such as hydrochloric acid, oxalic acid, lactic acid, and mixtures of these. The method is suitable for the estimation of small amounts of acidity, as, for example, in chyle.

W. J. W.

The Amalgamated Copper Cathode in Electro-analysis.

JOSÉ ALEMANY Y SELFA (*Anal. Fis. Quim.*, 1919, 17, 174—188).—The advantages in the use of mercury as cathode material in the electrolytic precipitation of metals are neutralised to some extent by the difficulties of manipulation. These difficulties are obviated by the use of the amalgamated electrode described. The cathode is of copper gauze, 5.5×11 cm. On this is deposited about 1 gram of silver by electrolysis in alkaline silver cyanide solution. The cathode is then amalgamated by electrolysis in mercurous nitrate solution until 0.8—1.5 gram of mercury has been deposited. It is then washed with water, alcohol, and ether. In combination with this cathode a rotating anode of platinum or of iron is employed. The temperature of electrolysis must not exceed 45° . A detailed account of the following electrolytic estimations is given: zinc in alkaline, ammoniacal, and neutral solution in presence of nitrate; zinc in sulphuric acid solution; cadmium in ammoniacal solution in presence of nitrate; cadmium in sulphuric acid and in neutral solution. In all cases the results obtained were excellent.

W. S. M.

Graphic Representation of the Chemical Composition of Natural Waters. ENRIQUE HERRERO DUCLOUX (*Anal. Fis. Quim.*, 1917, 15, 477—483).—The analytical results are graphically represented in relation to a regular hexagon of reference. The amounts of the six commonly occurring cations, Fe^{III} , Al^{III} , Ca^{II} , Mg^{II} , K^{I} , Na^{I} , are measured off in an invariable order along the six axes radiating from the centre of the hexagon through the vertices and the points thus marked off are joined. The six anions, SiO_3^{II} , SO_4^{II} , HCO_3^{I} , Cl^{I} , NO_3^{I} , HS^{I} , are similarly treated. The chemical

composition of the water is completely represented by the two irregular hexagonal figures so formed. W. S. M.

Chemical Analysis with Membrane Filters. RICHARD ZSIGMONDY and GERHART JANDER (*Zeitsch. anal. Chim.*, 1919, **58**, 241—280).—The membrane filters described by Zsigmondy and Bachmann (A., 1918, ii, 307) may be used generally in analysis; the filtration is rapid, the precipitate is washed readily, and very fine crystalline or colloidal precipitates are retained completely by the filters. The membrane is mounted for use in the apparatus (flanged funnel, perforated disc and ring) described previously by Zsigmondy (A., 1913, ii, 857). W. P. S.

Estimation of Small Quantities of Alkali Iodides in the Presence of Bromides and Nitrites. ED. LASAUSSE (*J. Pharm. Chim.*, 1919, [vii], **20**, 177—181).—The nitrite is oxidised by potassium permanganate in phosphoric acid solution at 40°; sodium hydrogen sulphite is then added to reduce chlorates and bromates, and the solution is boiled with the addition of potassium hydroxide and potassium permanganate; the iodide is thus converted into iodate, whilst the chloride and bromide are not affected. The iodate is then determined iodometrically. [See, further, *J. Soc. Chem. Ind.*, 1919, 899A.] W. P. S.

Estimation of Iodine in Cuprous Iodide. ED. LASAUSSE (*J. Pharm. Chim.*, 1919, [vii], **20**, 181—183).—Two methods are described. In the first, the cuprous iodide is decomposed with ferric chloride solution, the liberated iodine dissolved in carbon disulphide, and the solution separated and titrated. In the second method, the cuprous iodide is boiled with potassium hydroxide solution, and the resulting potassium iodide estimated in the solution by oxidation to iodate by means of potassium permanganate in alkaline solution, as described in the preceding abstract. [See, further, *J. Soc. Chem. Ind.*, 1919, 899A.] W. P. S.

Modified Benedict Method for the Estimation of Sulphur in Feeds, Faeces, and Foods. J. O. HALVERSON (*J. Amer. Chem. Soc.*, 1919, **41**, 1494—1503).—The following modified Benedict method for the estimation of sulphur in foods and faeces is described. About 3.44 grams of faeces or 2.7476 grams of cattle food are rolled up in half a filter paper and placed in a 300 c.c. Kjeldahl flask. Ten to fifteen c.c. of hot water are added, and the flask heated on a steam-bath with slight shaking, 20 c.c. of a mixture of concentrated and fuming nitric acid (1:4) are added, the flask stoppered with a small funnel, and kept for twelve hours. It is then placed on a steam-bath and digested for four days with occasional shaking. At the end of that time, a further 10 c.c. of the acid mixture are added, and the digestion continued until the solution is clear, when it is transferred in portions to a 60 c.c. evaporating basin and treated with 20 c.c. of the Benedict reagent during evaporation to complete dryness on the steam-bath. It is

then slowly baked on a sand-bath. The blackened residue is heated until it fuses, and then the temperature is lowered so that it solidifies slowly. About 20 c.c. of (1:4) hydrochloric acid are added, and the mixture heated for fifteen minutes on the steam-bath. The clear solution is then filtered into a 250 c.c. beaker, made up to 100 c.c. with water, heated to boiling, and treated with 10 c.c. of boiling 5% barium chloride solution from a dropper; the addition should take four minutes. The precipitate is digested for two to three hours on a hot plate, and then kept cold for forty-eight hours and filtered. It is shown that when silica is present, the peroxide method has a tendency to give high results. When the silica is removed, the results agree with those of the Benedict method to the third decimal place.

J. F. S.

Gravimetric Estimation of Sulphate as Barium Sulphate.

I. M. KOLTHOFF and E. H. VOGELZANG (*Pharm. Weekblad*, 1919, **56**, 122—142).—A detailed investigation into the sources of error in the estimation of sulphate as barium sulphate. The solubility of barium sulphate is increased by the addition of acids or of salts, except in the case where barium ion or sulphate ion is supplied. Samples of barium sulphate prepared in various ways show differences in solubility depending chiefly on the size of the particles. The solubility in water at ordinary temperatures is negligible. The solubility figures obtained in hydrochloric acid solution for acid concentrations $N/1$, $N/2$, $N/10$ are, respectively, 54, 31, and 11 mg. per litre. At 90° , the solubilities in $N/1$, $N/2$, and $N/20$ -acid were 416, 265, and 77 mg. per litre respectively.

In the estimation, reduction of barium sulphate during ignition of the dry precipitate and filter was found to take place to a slight extent in a porcelain crucible, and to a considerable extent in platinum. This can be avoided by ignition of the moist filter. Simultaneous precipitation of other salts with barium sulphate is caused by: (1) "conglomerate formation"; (2) solid solution; (3) adsorption; (4) mixed crystals; (5) mechanical inclusion; (6) chemical reaction. With regard to (2) and (3), experiments showed that in acid solution barium sulphate did not absorb electrolytes; (4) is an improbable case, as the commonly occurring salts in the precipitation belong to a different crystallographic group. Impurities in the barium sulphate are accounted for chiefly by the reactions between the SO_4^{2-} ion and the intermediate ions of other salts (ternary electrolytes) present. Excess of barium chloride, for example, gives rise to the formation of BaCl^+ , which reacts thus: $\text{SO}_4^{2-} + 2\text{BaCl}^+ \rightarrow \text{Ba}_2\text{Cl}_2\text{SO}_4$. The error in this case is in excess. Potassium sulphate gives KSO_4^- , which with Ba^{2+} gives $2\text{KSO}_4 + \text{Ba}^{2+} \rightleftharpoons \text{BaK}_2(\text{SO}_4)_3$, giving an error in defect (Richards and Parker, A., 1895, ii, 370). The occlusion of barium chloride can be avoided to some extent by precipitation in dilute solutions and at as high a temperature as possible, conditions unfavourable to the formation of complex ions. The assertion of Allen and Johnston (A., 1910, ii, 650) that $\text{Ba}_2\text{Cl}_2\text{SO}_4$ can be freed from

chlorine by ignition could not be confirmed, as the presence of chloride was proved in all cases after fusion of the precipitate with carbonate. Similarly, the statement of Pregl ("Die quantitative organische Mikroanalyse," 1917, p. 29) that occluded barium chloride can be washed out after ignition of the precipitate, could not be confirmed. The authors recommend results to be corrected for the presence of chloride by fusion of the precipitate with sodium carbonate and estimation of the chlorine. The presence of nitrate gives rise to a greater error than chloride. Errors due to the occlusion of calcium, iron, and potassium are chiefly to be ascribed to the formation of complex ions. Phosphate is precipitated as barium phosphate along with the sulphate. The authors are of opinion that it is impossible to give general directions for the accurate estimation of sulphate in solutions. W. S. M.

Estimation of Sulphate as Strontium Sulphate. I. M. KOLTHOFF and E. H. VOGELZANG (*Pharm. Weekblad*, 1919, 56, 159—161).—Following on their work on the precipitation of sulphates as barium sulphate (see preceding abstract), the authors have investigated the estimation of sulphate as strontium sulphate. Preliminary solubility determinations showed that strontium sulphate is practically insoluble in 50% ethyl alcohol. The sulphate is precipitated in the cold by 10% strontium chloride solution. An equal volume of 96% ethyl alcohol is added, and, after settling at the ordinary temperature, the precipitate is collected and washed with 50% alcohol. The moist filter is burned and ignited. Estimations were carried out in neutral solutions and in presence of hydrochloric acid, sodium acetate, ammonium chloride and nitrate, potassium chloride, sodium chloride and nitrate. Considerable errors in defect were observed. To eliminate the simultaneous precipitation of iron salts, sugar, glycerol, lactic and oxalic acids were added. These rendered filtration difficult without improving the results. The authors conclude that, in general, accurate results are not to be expected from this method. W. S. M.

Modifications of Pearce's Method for Arsenic. JOHN WADDELL (*J. Ind. Eng. Chem.*, 1919, 11, 939—941).—The following alterations are made in Bennett's and Canby's modifications of Pearce's method (A., 1899, ii, 519) in order to render them trustworthy. In Bennett's method, nitric acid should be added to neutralise any large excess of alkali in the solution, the latter then rendered slightly alkaline with sodium hydroxide, and acidified very slightly with acetic acid before the arsenic is precipitated as silver arsenate. Canby's method is modified in a similar way, except that in place of acetic acid, nitric acid is added in slight excess, and, after the addition of silver nitrate, this excess is neutralised by zinc oxide. W. P. S.

Reaction between Arsenious Oxide and Iodine. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 621—634).—The reaction $\text{As}_2\text{O}_3 + 2\text{I}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{As}_2\text{O}_5 + 4\text{HI}$ is studied with reference to the

limits of hydrogen-ion concentration within which a definite end-point is obtained. The hydrogen-ion concentration is determined colorimetrically by means of various indicators. In the titration of $N/10$ - and $N/100$ -arsenious oxide solutions with iodine, the final acidity must lie between $10^{-11.0}$ and $10^{-5.0}$ mol. hydrogen ion per litre. In the titration of $N/10$ - and $N/100$ -iodine solutions with arsenious oxide solution, the initial limits are $10^{-9.0}$ and $10^{-5.5}$, and the final $10^{-8.0}$ and $10^{-5.0}$. The purity of the arsenious oxide used is best estimated by measurement of the conductivity of a saturated solution. The commonly occurring impurity is arsenic oxide, which may be estimated by means of the reaction of the solution with dimethyl-yellow and methyl-red. Neutral or weakly acid solutions of arsenious oxide are stable, and may be kept indefinitely without change of titre. In alkaline solutions, oxidation of arsenious to arsenic oxide takes place.

W. S. M.

Method for Estimation of Carbon by Wet Combustion, using Barium Hydroxide as Absorbent. P. L. HIRSHARD

(*J. Ind. Eng. Chem.*, 1919, 11, 941—943).—A convenient method of procedure and apparatus for use in the method are described. The substance is oxidised by heating in a flask with chromic acid and sulphuric acid, and the resulting carbon dioxide is carried by a current of air into an excess of standard barium hydroxide solution; at the end of the operation, the excess of barium hydroxide is titrated with hydrochloric acid, using phenolphthalein as indicator. The air used is first passed through a soda-lime tube; after leaving the oxidation flask, the air carrying the carbon dioxide, etc., passes through a condensing tube, a tube filled with beads moistened with sulphuric acid, and a tube filled with amalgamated granulated zinc, before it enters the barium hydroxide solution; the latter is contained in an inclined flask, into which extends the lower end of a Meyer bulb tube.

W. P. S.

Microchemical Identification of Lead. G. DENIGES (*Bull. Soc. Pharm., Bordeaux*; from *J. Pharm. Chim.*, 1919, [vii], 20, 153—160).

—Soluble lead salts yield characteristic crystals of lead iodide when treated with a drop of potassium bromide solution and a drop of potassium iodide solution. With insoluble lead salts, the addition of a drop of sulphuric acid is necessary. Lead chromate, cyanide, and fluoride should be evaporated with hydrochloric acid, and metallic lead and lead sulphide with nitric acid, before the test is applied.

W. P. S.

Titrimetric Estimation of Lead. PAUL HOLMSEN (*Tidskr. Kemi*

Farm. Ter., 1919, 16, 110—113).—A solution, not exceeding 100 c.c., containing 0.5—0.1 gram of lead, neutralised with ammonia, is acidified with 15 c.c. of acetic acid, 10 grams of ammonium acetate added, and the liquid warmed to 70—80°. The lead is precipitated by slowly adding 10 c.c. of ammonium molybdate solution, with constant stirring, warming for fifteen minutes, setting aside for thirty minutes, filtering, and washing with hot

water. The precipitate is treated with 50 c.c. of dilute sulphuric acid and hot water, 10 grams of pure zinc added, and boiled for ten minutes, filtered, washed with hot water, and the molybdenum in the filtrate titrated with 0.1*N*-permanganate. One c.c. of 0.1*N*-permanganate is equivalent to 0.007296 gram of lead.

CHEMICAL ABSTRACTS.

Microchemical Reactions with Thiosulphuric Acid. A. BOLLAND (*Compt. rend.*, 1919, **169**, 651—654).—Sodium thiosulphate gives crystalline precipitates, which are well defined when examined microscopically, with thallous nitrate, barium chloride, lead acetate, and benzidine. Sketches are given of the microcrystalline structure of these precipitates. In the case of barium chloride, the appearance of the precipitate varies with the experimental conditions. It is preferable, in this case, to use a concentrated solution of the thiosulphate.

W. G.

Electroanalysis of Copper without Platinum Electrodes. JUAN GUIERAS (*Anal. Fis. Quim.*, 1919, **17**, 209—216. See A., 1915, ii, 652, and 1916, ii, 199).—A copper cathode and a rotating anode of passive iron were employed. 0.1—0.2 Gram of electrolytic copper was dissolved in twenty drops of nitric acid for each estimation, and the various electrolytes were prepared by the addition of the following solutions: (1) 5 grams of disodium phosphate in water and 15 c.c. of concentrated ammonia solution; (2) 5 c.c. of 50% ammonium acetate solution and 15 c.c. of ammonia; (3) 3 grams of ammonium oxalate in water and 15 c.c. of ammonia; (4) 15 c.c. of formic acid solution (75 c.c. of water and 25 c.c. of formic acid, D 1.2) and 15 c.c. of ammonia; (5) 2 grams of citric acid in water and 15 c.c. of ammonia; (6) 2 grams of boric acid in water and 15 c.c. of ammonia. During electrolysis, the electrolyte was kept warm and the voltage gradually reduced from about 3 volts to 1.7—1.8 volts. The experiments were repeated with the constant voltage of one accumulator throughout. In all cases, the deposits on the cathode were coherent and the results satisfactory. Experiments in ammoniacal solutions of thiocyanate gave inaccurate results.

W. S. M.

New Separation of Aluminium and Vanadium. P. WENGER and H. VOGELSON (*Helv. Chim. Acta*, 1919, **2**, 550—553).—Methods are described for the quantitative separation of (1) aluminium and vanadium, (2) aluminium, iron, and vanadium. In the case of aluminium and vanadium the mixture of oxides is heated with six times its weight of anhydrous sodium carbonate, at first gradually, until the mass melts, and then at a higher temperature for three hours. The crucible and contents are allowed to cool somewhat, plunged into distilled water, and raised to the boiling point, when a clear solution of sodium aluminate and vanadate is obtained. The solution is made up to 500 c.c. with distilled water, raised to the boiling point, and treated with about ten times its weight of ammonium nitrate in small quantities. Aluminium hydroxide is pre-

precipitated, filtered, washed, ignited, and weighed as Al_2O_3 . The filtrate is acidified with hydrochloric acid, neutralised with ammonia, raised to the boiling point, and treated with barium chloride solution. Barium vanadate is precipitated; the precipitate is kept for twenty-four hours, filtered, washed with cold water, dried, ignited, and weighed as $\text{Ba}(\text{VO}_3)_2$. In the presence of iron a solution is made which is precipitated cold by ammonia. This precipitate, which contains iron and aluminium hydroxides and ammonium vanadate, is filtered, washed, ignited in a platinum crucible, mixed with six times its weight of sodium carbonate, and ignited as before. The fused mass is dissolved in water to which 1 gram of sodium carbonate has been added. The iron left insoluble as oxide is filtered off and weighed, and the filtrate treated as described above. The results of the analyses are extremely good. J. F. S.

Sulphite Method for the Separation and Estimation of Gallium when Associated with Zinc. LYMAN E. PORTER and PHILIP E. BROWNING (*J. Amer. Chem. Soc.*, 1919, **41**, 1491—1494).

Gallium is conveniently precipitated from neutral or acid solutions of zinc by adding 4 or 5 c.c. of ammonium hydrogen sulphite solution (made from 1:4 ammonia) to 200 c.c. of the zinc solution and boiling. If gallium is present it will be precipitated in granular form and can be filtered and washed by decantation. The precipitate is dissolved in a few drops of hydrochloric acid, diluted to 200 c.c. with water, and reprecipitated as before. This is filtered, washed, ignited, and weighed as Ga_2O_3 . The potassium ferrocyanide test is sensitive to 0.0002 gram of gallium, and may be used to detect this element in the presence of zinc. If sodium or ammonium hydrogen sulphite is added to such a cold solution and then potassium ferrocyanide, there will be no precipitation, but on the addition of a few drops of hydrochloric acid the gallium will be precipitated, but not the zinc. J. F. S.

Hydrochloric Acid Colour Method for Estimating Iron.

J. C. HOSTETTER (*J. Amer. Chem. Soc.*, 1919, **41**, 1531—1543).—A method has been elaborated by which the yellow colour produced by dissolving ferric chloride in hydrochloric acid may be used for the estimation of iron. This involves the comparison of the tint with standard tints. The temperature-coefficient for the colour varies 2—3% per degree, depending on the concentration of the iron and probably also on the acidity. The colour developed by a given amount of iron varies with the acid concentration, reaching the maximum intensity at 26—28% of hydrochloric acid. The relative increase produced by acid is greater the higher the concentration of iron; this is especially true above 20% of hydrochloric acid, but below this concentration the relative change is independent of the iron content. Inasmuch as solutions must frequently be boiled in order to ensure complete solution of the iron present as "scale," the use of constant boiling acid is recommended, and its use has been found to be altogether satisfactory. The effect of salts on the colour indicates that sulphates cause bleaching and chlorides intensification; a detailed study of the effect of calcium chloride

shows that an intensification of 2.5 may be attained by the addition of this salt; consequently, when testing for iron in a very soluble chloride the standard iron solution must be made up to the same salt concentration. J. F. S.

A Method for the Quick Estimation of the Nickel-Iron in Meteorites. G. T. PRIOR (*Min. Mag.*, 1919, 18, 349—353).—The classification of meteorites based on the amount of nickel-iron they contain and the ratio of iron to nickel in this metallic portion (A., 1916, ii, 635) requires a rapid method applicable to meteoric stones for the estimation of these quantities. The sieved material is separated into attracted and unattracted portions by a magnetic comb. The former is digested with dilute aqua regia, and the insoluble silicate which was entangled with the metal separated off; estimations of the silica and sulphur give the amounts of the soluble silicate (olivine) and the troilite (FeS); these, deducted from the weight of the attracted portion, give the weight of the nickel-iron. Nickel is estimated by precipitation with dimethylglyoxime in an aliquot portion of the solution. The method is applied to the partial analysis of seventeen meteoric stones, and the results (percentage of nickel-iron, and ratio of Fe+Co:Ni) are tabulated. L. J. S.

Electroanalysis of Nickel without Platinum Electrodes. EMILIO FERNÁNDEZ-ESPINA (*Anal. Fis. Quim.*, 1919, 17, 199—205. See A., 1916, ii, 494).—A copper cathode and a rotating iron anode, rendered passive by immersion in nitric acid, were employed. About 0.1 gram of pure nickel was dissolved in 15 drops of nitric acid and the solution evaporated to dryness after the addition of 18 drops of sulphuric acid. The various electrolytes were prepared by the further addition of the following to the nickel sulphate thus obtained: (1) sodium phosphate solution and 10 c.c. of concentrated ammonia solution; (2) 5 c.c. of 50% ammonium acetate solution and 10 c.c. of ammonia; (3) 15 c.c. of 25% formic acid and 15 c.c. of ammonia; (4) 5 grams of ammonium oxalate in 15 c.c. of water and 15 c.c. of ammonia; (5) 2 grams of crystallised boric acid and 15 c.c. of ammonia; (6) 2 grams of tartaric acid and 10 c.c. of ammonia. In each case a convenient quantity of water was also added. During the electrolysis the electrolyte was kept slightly warm, and the current increased progressively from 0.4 ampere to about 0.8 ampere. The results were moderately satisfactory in all cases except the last, in which the iron of the anode appeared to be dissolved and deposited with the nickel. W. S. M.

Estimation of Tin. F. LE NAOUR (*Ann. Chim. anal.*, 1919, [iii], 1, 308—309).—The author finds that ignited stannic oxide (SnO_2) is not appreciably hygroscopic, although Bertiaux has stated the contrary (A., 1918, ii, 408). One gram of the oxide absorbed only 2 mg. of moisture when exposed to the atmosphere for eighteen hours. W. P. S.

The System *n*-Butyl Alcohol-Acetone-Water. JOSEPH REILLY and EDGAR W. RALPH (*Sci. Proc. Roy. Dublin Soc.*, 1919, 15, 597—608).—The densities of a series of *n*-butyl alcohol-acetone-

water mixtures have been determined, and graphs from these prepared with rectangular and triangular co-ordinates. From these results the composition of an unknown mixture may readily be obtained with a fair degree of accuracy if a density determination and the estimation of one constituent are made. The limit of solubility of *n*-butyl alcohol in water at 20° is 7.9% and of water in *n*-butyl alcohol 20%. The maximum contraction for mixtures of *n*-butyl alcohol and water within the range of solubility at 20° is 0.74%.

Acetone and *n*-butyl alcohol are miscible in all proportions, there being a slight increase of volume on mixing. W. G.

Estimation of Methyl Chloride in Gas Mixtures. V. C. ALLISON and M. H. MEIGHAN (*J. Ind. Eng. Chem.*, 1919, 11, 943—946).—The method proposed depends on the solubility of methyl chloride in glacial acetic acid, and is particularly useful for estimating the proportion of methyl chloride in chlorinated natural gas. A measured volume of the gas is led six times into a Hempel pipette containing glacial acetic acid, and then returned to the measuring burette; the contraction in volume gives the quantity of methyl chloride present. One volume of acetic acid absorbs more than 40 volumes of methyl chloride and 4 volumes of natural gas, but the solubility of the latter is very small when the gaseous mixture contains 40% or more of methyl chloride. The results obtained agree with those found by the partial pressure method (A., 1915, ii, 100). W. P. S.

Sulphonal. A. FALCK (*Pharm. Zentr.-h.*, 1919, 60, 409—416).—The solubility of sulphonal in various solvents was found to be as follows, the figures representing grams of solvent required to dissolve 1 gram of the substance: Water at 15°, 423; water at 100°, 8; 90% alcohol at 15°, 60; ether at 17°, 79; chloroform at 20°, 3.3; methylene chloride, 2.8; benzene at 17°, 12.7; ethyl acetate, 13.7; toluene, 19.3; carbon tetrachloride, 110; carbon disulphide, 440; 2% sodium chloride solution at 18°, 440. Owing to the fact that sulphonal begins to volatilise at 60° and is very appreciably volatile in the presence of water-vapour, solutions containing the substance should not be concentrated by evaporation before the quantity of sulphonal is estimated. The sulphonal should be extracted with chloroform and the extract evaporated at a low temperature. Sulphonal is stable for a long time in the presence of decomposing organic matter, and characteristic crystals may be obtained from its ether or chloroform solution. W. P. S.

The Estimation of the Volatile Fatty Acids by an Improved Distillation Method. JOSEPH REILLY and WILFRED J. HICKINBOTTOM (*Sci. Proc. Roy. Dublin Soc.*, 1919, 15, 513—538).—It is known that when dilute solutions of organic fatty acids are distilled certain regularities are observed. Various forms of distillation constants have been suggested by Duclaux (A., 1896, ii, 504), Naumann and Müller (A., 1901, i, 204), and Stein (A., 1913, ii, 670)

to express such regularities. These constants may be derived from Nernst's law of distribution, and on this law the authors base a discussion of the theory of distillation of dilute solutions. A method of distillation at constant volume, in which only small changes in concentration occur, is recommended, and an apparatus is described in which this process may be simply and satisfactorily carried on. The distillation constants of the fatty acids from formic to octoic have been determined, and it is shown that there is a definite relationship between the rate of distillation and the molecular constitution of these acids. Acids containing a branched carbon chain have higher constants than normal acids of the same molecular weight.

The methods of calculation are quite satisfactory for establishing the identity and purity of a solution of a single volatile fatty acid, and also give fairly accurate results in the analysis of "two-acid" mixtures. The results with mixtures of three acids are not so satisfactory. The method may be applied to fermentation products. By suitable modification of the apparatus the distillation constants for the volatile acids in butter and coco-butter can be determined and utilised for detecting the presence of adulterants.

W. G.

Estimation of Lactic Acid by Oxidation. O. SCHUPPLI (*Mitt. Lebensmittelunters. u. Hyg.*, 10, 44—47; from *Chem. Zentr.*, 1919, ii, 894).—Szeberényi's process (A., 1918, ii, 138) gives trustworthy results in aqueous solution, but is not applicable to wines.

H. W.

Naphtharesorcinolcarboxylic [1:3-Dihydroxynaphthalene-2-carboxylic] Acid as a Reagent for Glycuronic Acid. Y. ASAHINA and C. HASEGAWA (*Yakugakuzasshi [J. Pharm. Soc. Japan]*, 1919, No. 448, 484—489).—1:3-Dihydroxynaphthalene-2-carboxylic acid, which cannot be preserved unchanged for any length of time, is best kept in the form of the barium salt, from which it is prepared, when required, by treatment with hydrochloric acid. The authors also describe the preparation of this reagent from phenylacetic acid by Metzner's method (A., 1898, i, 152).

CHEMICAL ABSTRACTS.

Detection of Small Amounts of Chloral in the Presence of Chloroform and Formalin Embalming Fluid. A. O. GETTLER (*Proc. Soc. Exp. Biol. Med.*, 1919, 16, 110—116; from *Physiol. Abstr.*, 1919, 4, 255).—When kept at the ordinary temperature for half an hour with sodium carbonate and phloroglucinol, chloral develops lilac to orange, to blood orange, to deep red colorations, the shade depending on the amount of chloral present. Chloroform does not give this reaction; formaldehyde and acetaldehyde give a red colour. With resorcinol and sodium carbonate, chloral gives a red colour and a green fluorescence, the latter even in dilute solution; chloroform does not yield the green fluorescence, whilst substances of an aldehydic character do not give the reaction.

H. W.

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